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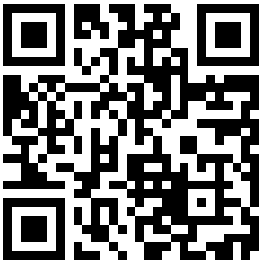

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THE PRODUCTION OF URANIUM BY THE REDUCTION OF UF_4 BY Mg

By: F. H. Spedding, H. A. Wilhelm, and W. H. Keller

June 26, 1945

ABSTRACT

Due to difficulties encountered in the production of calcium metal in adequate quantity and of adequate purity at low cost, it became desirable to replace calcium by a cheaper metal in the production of uranium. Because of the heats of formation of its compounds, its relative stability in air, and its cheapness in high purities, magnesium was was the best suited metal for the purpose. Since the heat of reaction of the reduction of UF_4 by Mg was not sufficient to melt the products, it was necessary to add heat to the system. This was done in experimental studies both by preheating the reactants before reaction was initiated and by the use of a simultaneous auxiliary reaction producing more heat than the primary reaction. For the latter purpose the reductions of $KClO_3$, $K_2S_2O_8$ and of other salts by Mg were suitable reactions. The use of "boosters" or auxiliary oxidants involved extra work and materials, thus increasing costs and offering additional opportunity for contamination, hence the preheating of the reactants was adopted for large scale production.

The reactants were mixed in a mechanical mixer, placed in steel reactors or "bombs" lined with high-calcium or fused dolomitic lime and preheated in a gas-heated furnace at 1150 to 1250°F for about 50 minutes, until reaction occurred. The products, U and MgF_2, were fused by the combined heat of reaction and the heat added by the furnace and collected as liquids in the bottom of the reactor. There they were separated by gravity into a pool of metal covered by a pool of slag. The metal solidified into a cylindrical ingot.

The purity and particle size of the UF_4 had much to do with the yield and condition of the metal. Over three per cent of UO_2 or UO_2F_2 caused an appreciable decrease of yield with 7 or 8% causing a large decrease. The salt gave best results when ground to 100 to 325 mesh, with not over 60% of -325 mesh.

Of various types of magnesium tested for their productivity in the process, that produced by the New England Lime Co., Canaan, Conn., by the ferrosilicon process gave most consistent results. It was found that the size distribution of Mg between 10 to 40 mesh had no great

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effect on the yield of uranium, but no significant quantity of +10 or -40 material could be tolerated. The excess of Mg used over theoretical was 7½% in the 6" bomb.

Much difficulty was experienced in securing properly burned lime for use in forming the refractory lining of the reactor or bomb. High-calcium lime secured from the Ste. Genevieve Lime Co., St. Louis, Mo., was of adequate purity and was usually well-burned, but even if properly burned, the lime had too great a tendency to pick up moisture from the air. After an extensive investigation of various refractory substances, electrically fused dolomitic lime was finally adopted as the lining material.

A preheat of 50 to 60 minutes at furnace temperatures varying from 1100 to 1250°F was found suitable for the 6 inch bomb charge, varying with raw materials and liner used. With average products a 50 minute preheat at 1200°F gave optimum results. The large scale production of thousands of tons of metal of consistently high purity was achieved. The metal averaged 99.9% in uranium content.

THE PRODUCTION OF URANIUM BY THE REDUCTION OF UF_4 BY Mg

Due to the urgent demand for at least limited amounts of uranium at the beginning of the project, the production of metal by the reduction of UF_4 by calcium was developed and put into operation before other procedures were fully investigated.(1) Reduction of the oxides with carbon and with metals had been investigated with no satisfactory results before the reduction of the fluoride was first attempted. Al gave partial reduction but Al_2O_3 could not be separated from the product. Ca produced only powdered metal. Nor did the first attempts at the reduction of the fluoride by other metals such as Mg or Na appear promising. Mg failed to produce enough heat to fuse the products and only powdered pyrophoric metal was obtained. Na gave only partial reduction and produced low yields in small pellets.

Based on Reports No. CC-238, CC-258, CC-298, CE-345, CT-422, CT-604, CT-609, CT-686, CT-751, CT-816, CT-891, CT-1180, A-1024, A-1036, A-1038 and A-1039.

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1. Experimental Reduction of UF_4 by Mg

After sufficient metal had been produced[1] by the use of Ca to meet the most pressing needs for the study of its properties and fabrication and for use in experimental piles, the problem of cost in the over-all picture became more important and the replacement of Ca by a cheap metal received consideration.

1.1 Disadvantages of Ca. In addition to high cost, the purity of the calcium was not as high as was desirable. It appeared that a more volatile element might be more completely purified by distillation. Both Mg and Na met these objections to Ca. The extreme difficulty of handling Na in quantity in disintegrated state in air made it very undesirable, however, regardless of any advantages in cost or purity and no further consideration was given to its use. Mg was available in great abundance, its comminution to the desired size could be handled like that of Ca, it was much more stable in air, its production by the ferrosilicon or the carbothermic processes yielded a very pure distilled product and its price had been pegged at 20½ cts/lb by W.P.B. Its only disadvantage was the lower energy of formation of its compounds as compared with those of Ca. Thus, if UF_4 were reduced, the heats of formation at 298°K of the fluorides produced per mole of UF_4 reducing with Ca, Na, Mg and Al are as follows:

2 CaF_2	$\Delta H = 2 \times -286.26 = -572.52$ Kcal
4 NaF	$\Delta H = 4 \times -136.30 = -545.20$
$2MgF_2$	$\Delta H = 2 \times -263.80 = -527.60$
1.33 AlF_3	$\Delta H = 1\ 1/3 \times -329.03 = -438.71$

The heat of formation of UF_4 is reported as -446 Kcal/mole at 298°K, hence on the basis of these data it appears probable that the above metals except perhaps Al should be able to reduce UF_4 under actual operating conditions.

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1.2 Reduction of UF_4 by Mg Without Addition of Heat. The reduction of UF_4 by Mg was first attempted[2] by mixing it with Ca in an effort to lower the melting point of the slag and to substitute at least part of the Ca by Mg to reduce costs. A mixture of a 57.5 mol per cent Mg and 42.5 mol per cent Ca was used producing a slag having the composition of the eutectic mixture of CaF_2-MgF_2. The mixture was used in 50 per cent excess over the theoretical weight required to reduce the charge of 942 g of UF_4. The charge was ignited by electrically heated fuse wire. A compact button of metal was obtained representing a yield of only 30 per cent, far less than the Ca alone should have produced. An attempted reduction by Mg alone resulted in only partial reduction to powdered pyrophoric metal. No pellets were obtained. An alloy containing 78 per cent Ca and 22 per cent Mg, crushed to about 10 mesh particles, produced a yield of U of 62 per cent.

In November, 1942, therefore, further experiments were undertaken in the use of magnesium as the reductant.[3] A repeated attempt at reduction on the 4" bomb scale under optimum conditions ignited locally by electrically heated fuse wire again yielded only pyrophoric powdered metal. It was obvious that even on a considerable scale more heat would have to be supplied to fuse the products of the reaction.

1.3 Addition of Heat to System. The simplest way to add heat to the system is to preheat the reactants before reaction begins. This procedure is used in preheating gases in many processes as in the blast furnace and was used in the earliest experiments at Iowa State College with oxides and with UF_4.[4] The final heat available in the system is then the sum of the heat added in preheating plus the heat of reaction minus the radiation heat losses. It might therefore be possible to produce massive uranium by the use of magnesium as reductant by heating the entire charge in the bomb in a furnace or soaking pit until reaction occurred instead of igniting locally by a fuse, provided reaction was not initiated before enough had been added in this fashion. In case too much heat were added before ignition occurred, sufficient heat could be added by preheating only to a given temperature, then initiating the reaction locally by a fuse as before.

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1.4 Addition of Heat by Preheating. For this purpose a charge of 2016 g of UF_4 was mixed with 400 g of Mg, representing an excess of 30 per cent, the charge placed in a steel bomb(3) with high-calcium lime liner and heated in a chromel-wound resistance furnace at about 650°C. Reaction occurred at 640°C (outside bomb temperature) and a yield of 80.5 per cent of clean, compact massive metal was obtained. In similar successive experiments yields of 80 to 95 per cent were obtained. This procedure was expanded at Iowa State College and adopted at other plants as the process by which most of the metal used on the project was produced.

1.5 Addition of Heat by Booster. Another procedure by which heat might be added to a system is by conducting simultaneously an auxiliary reaction. Thus in the thermite process auxiliary combustions are used to bring reactants up to necessary temperatures. The final heat available to the system, which is equal to the sum of the heats of the two reactions, may be sufficient to bring the products into the desired state such as the molten state of metal and slag. The use of such a process requires that the products of the auxiliary reaction will be separable or removable from the main product or will be in no way deleterious.

The addition of an oxidant which can be reduced by reductant already in use is desirable. Decomposable salts which supply oxygen, such as chlorates or sulfates, peroxides such as lead dioxide or barium dioxide, binary salts supplying considerable heat on reduction such as halides of most metals, or oxidizing elements themselves such as iodine, bromine or sulfur could readily be used as auxiliary oxidants or "boosters", as they were designated on the project.

Some of the additional problems created by the addition of other substances to the system in the use of "boosters" in the bomb process were:

(a) Purity. No substance could be used containing an element whose presence could not be tolerated in the final product unless that element could be completely removed during processing.

(b) Pressure. No "booster" could be used which produced gaseous or volatile final products which with the sudden increase of temperature on reaction would produce pressures beyond the limits of the heated bomb.

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(c) Handling. Gaseous boosters such as chlorine, which offered difficulty in introduction into the bomb, were undesirable although usable. Hygroscopic materials requiring special handling as in dry rooms, etc., were undesirable but usable.

1.5.1 $KClO_3$ as Booster. From the point of view of convenience of handling, permissibility of end-products and heat production potassium chlorate looked very favorable as a booster in the reduction with magnesium. All by-products, KCl and CaO would be removed in the slag. Any potassium reduced to metal could be distilled out by remelting in vacuo.

As an estimate of the quantity of $KClO_3$ required for an experimental reaction, it was assumed that the heat produced by the reduction of UF_4 by Ca was the quantity needed for the fusion of the products to permit their separation. In the reduction of UF_4 by Mg the heat of fusion of the U remains the same, the heat of fusion of MgF_2 is very nearly that of CaF_2 and the only difference would be the heat needed to volatilize the excess Mg, since the Ca excess was not volatilized to an equal extent at the temperature reached. The heats of reaction of the two reductions are as follows:

$$\underset{-446}{UF_4} + 2\ Ca \longrightarrow \underset{-580}{2\ CaF_2} \qquad \Delta H = -134\ Kcal$$

$$\underset{-446}{UF_4} + 2\ Mg \longrightarrow U + \underset{-528}{2\ MgF_2} \qquad \Delta H = -82\ Kcal$$

Thus it appears that 52 Kcal additional heat is needed for compensating for deficiency of heat in the Mg reaction as compared with the Ca reaction plus 19 Kcal for vaporizing 0.4 mole Mg (30% excess). Additional heat will be needed for the fusion and heating of products of the booster reaction, but these will be relatively small and may be ignored in the first approximation.

The heat of reaction of the reduction of $KClO_3$ by Mg based on heats of formation at 298°K is -452 Kcal/mole $KClO_3$.

$$\underset{-90}{KClO_3} + 3\ Mg \longrightarrow \underset{-104}{KCl} + 3\ \underset{-438}{MgO} \qquad \Delta H = -452$$

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To add sufficient heat to make the total heat production of the Mg reaction equal that of the Ca reaction and hence reach the same final temperature thus requires 71 Kcal/452 Kcal per mol $KClO_3$ = 0.157 moles $KClO_3$ per mole of UF_4 used, or about 1 mole $KClO_3$ per 6.5 moles UF_4. The heat required for fusing $KClO_3$, raising its temperature to 600°C and heating the KCl from 600°C to 1500°C (approximate final temperature) is about 5 Kcal. Then 76 Kcal/452 Kcal/mole $KClO_3$ = 0.168 moles $KClO_3$ or 1 mole $KClO_3$ per 6 moles of UF_4. Since the behavior of the chlorate under the bomb conditions was not too predictable, one mole of $KClO_3$ per 7 moles of UF_4 was first tried.

In the first experiment 440 g of UF_4, 24.5 g of $KClO_3$ representing 1/7 mole $KClO_3$ per mole UF_4 and 109 g Mg representing 33 per cent excess over that required for reduction of the UF_4 and the $KClO_3$ were mixed and charged into a lime-lined steel bomb equipped with electrically heated fuse as was used in the calcium process. The reaction was initiated by the fuse and proceeded normally. A yield of 80.4 was obtained.(3)

The ratio of $KClO_3$ to UF_4 was examined from 0.1 to 0.25 moles $KClO_3$ per mole of UF_4 but the originally calculated 0.14 moles $KClO_3$ per UF_4 or 1 mole of $KClO_3$ per 7 moles UF_4 was found to be optimum for the scale used. This told exactly the additional heat needed in the Mg reduction over the Ca reduction under the operating conditions. It must be bourne in mind that the efficiency of heat utilization is a function of scale of operation as well as of shape of equipment, hence this figure does not apply to greatly different charges or differently shaped vessels.

1.5.2 Other Boosters. Magnesium persulfate was also used with success as a booster with magnesium.(4) On the basis of comparison with the $KClO_3$ requirements, it was calculated that 1 mole $K_2S_2O_8$ per 14 moles of UF_4 should supply the required amount of additional heat. A reduction on this basis with 20 per cent excess Mg produced a yield of 96 per cent. The odor of H_2S from the ingot was very pronounced, but no odor of SO_2 was observable from the bomb immediately after reaction.

Later iodine was used with calcium on small scale reductions(5) and a number of different auxiliary reactions have been used in the preparation of different metals.(6)

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Of the two procedures successful in producing massive metal with magnesium the preheat had several advantages over the use of "boosters". The fewer substances used in a reduction the less is the chance of contamination, the less handling, storage and preparation of materials are required, the less labor is involved in preparing and loading the charge and the greater is the production per unit operation. The use of certain boosters adds some danger by an instantaneous increase in pressure if a gaseous intermediate is produced before the reaction is completed even though there be no gaseous product in the end. For these reasons production by the magnesium process was begun by the preheating method and has continued so to the present time.

2. Final Production Line Procedure in Reduction Stage at Iowa State College

Following the successful reduction of UF_4 by Mg the adoption of the process in production was immediately planned. Large scale experimentation was begun for determining the specifications of satisfactory materials and for establishing optimum operating conditions for the process. In order that the reader may better understand the experimental procedures employed for these purposes and the results obtained, the method of performing the reduction will first be described. The reactants were mixed in proper proportion and caused to react in a steel reaction chamber or "bomb" (Fig. 1) lined with a refractory oxide. Reaction was initiated by heating the closed bomb in a gas-heated furnace or soaking pit maintained at 1050 to 1300°F varying with condition to be discussed below. The production line procedure in use at Iowa State College at the time of the peak of production was as follows:(7)

2.1 Construction of Bomb. The bomb was constructed of standard 6" pipe with a welded bottom of 3/8" steel plate and fitted with a standard companion flange at the upper end, which was threaded. It was covered by a second companion flange closed with a standard pipe plug. The refractory lining consisted of a layer of ground, electrically fused dolomitic lime applied by jolting into the annular space between a steel mandrel placed concentrically within the bomb and the bomb wall.

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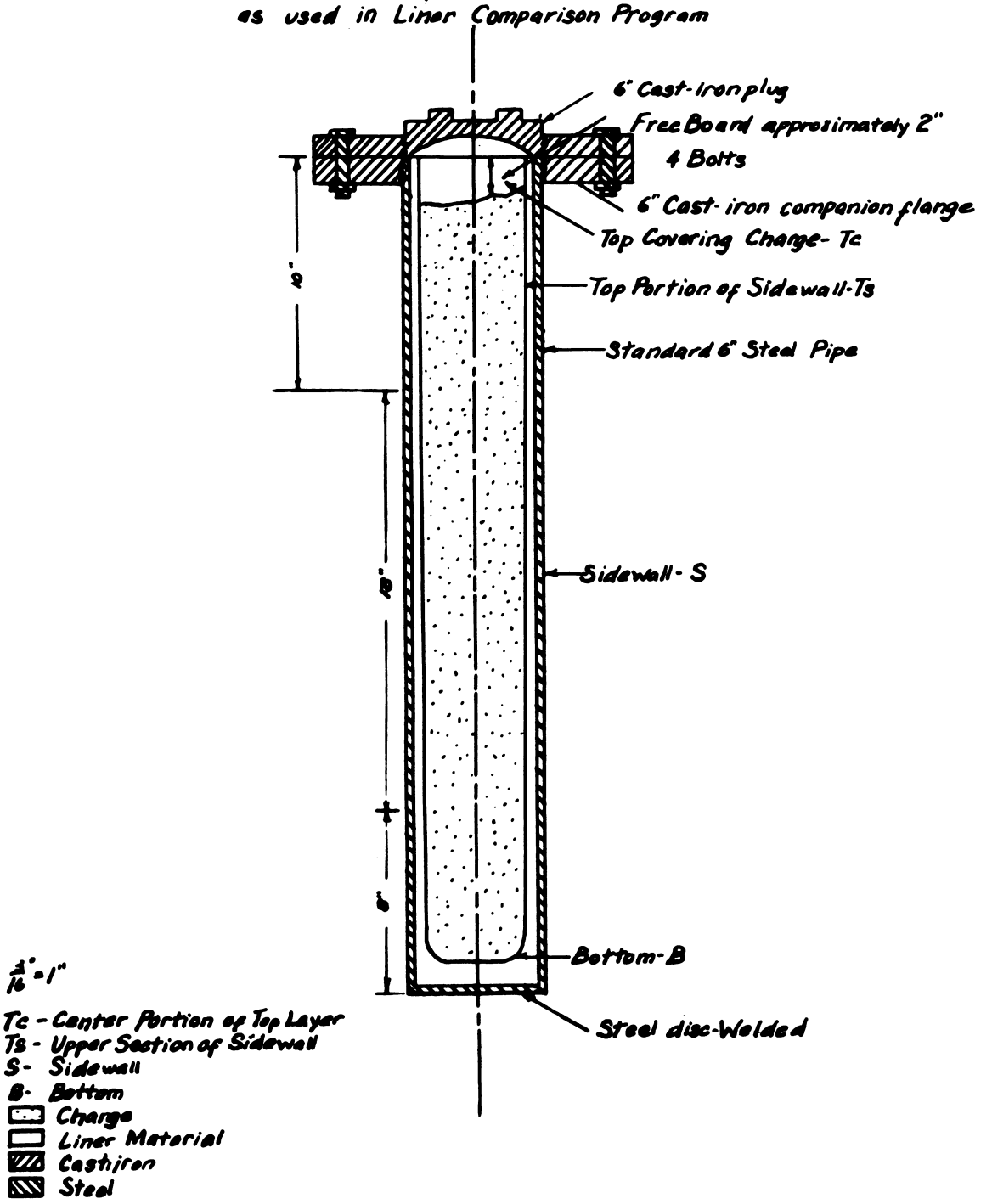
Figure 1

Sections of Liner Wall
as used in Liner Comparison Program



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2.2 Installation of Refractory Liner. The procedure for applying the liner was as follows: Sufficient refractory (2-2½ lbs) was poured into the bottom of the bomb and jolted by hand into position to form the bottom layer of the liner. The mandrel was made of seamless steel tubing with a welded plug in the bottom machined to shape and chromium plated. For the 6" bomb the mandrel was 40" long, 5 1/8" diameter at the top tapering to 5" diameter at the bottom. The annular space between mandrel and bomb was then filled with E.F.D. (electrically fused dolomite) by pouring into a funnel which fitted around the mandrel and just inside the bomb. The mandrel was kept centered during this period by observation. The bomb was then jolted on an "Arcade" jolting table with 4" piston. As soon as this portion of the wall was somewhat compacted more lime was added and jolting continued. This process was continued until the liner had been completed to the top of the bomb. A steel ring 3/8" thick which fitted exactly between the mandrel and bomb was placed on top of the upper surface of the liner to supply pressure during the final jolting. The forming of a 6" bomb liner required about 15 minutes of jolting at the approximate rate of 3 blows per second at an air pressure 75 to 90 psi on the piston.

Before removal of the mandrel the stopper was removed from an air hole or vent which extended through the mandrel from top to bottom. Without such a vent the suction created by the loosening and removal of the mandrel always caused the liner to break and cave in. The hole was closed during jolting by a steel rod which passed through the mandrel and fitted tightly at the bottom and conformed to the surface of the mandrel.

The mandrel was removed by fixing the bomb rigidly in position and withdrawing the mandrel with very even pressure by a chain hoist on the monorail above the loading line. It was essential that the mandrel not be permitted to swing and strike the liner during removal.

2.3 Weighing and Mixing of Charge. The reaction mixture or charge consisted of 56 lbs. of -100 mesh UF_4 and 9 lbs., 4 oz. of -10 mesh magnesium representing an excess of 7½ per cent above the stoichiometric weight. These reactants properly prepared as described in the following

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sections were mixed in a motor-driven MacLellan batch mixer of one cubic foot capacity. The mixer was operated at about six revolutions per minute for 4 to 5 minutes.

2.4 Introduction of Charge into Bomb. The mixed charge was poured into the bomb by lowering the latter into a pit on the floor, rolling the mixer directly over the bomb and pouring the charge into the bomb through a telescopic funnel so constructed as to prevent damaging the liner either by the introduction of the funnel or by the falling charge. This device consisted of two cylinders, the outer being 4" o.d., 3½" i.d., 14" long, rigidly supported by arms fitting into the bolt holes of the flange and extending 8" above the top of the bomb. This cylinder acted as a support and guide for the inner cylinder which was 3 3/8" o.d., 3" i.d., 32" long with a sheet steel funnel about 12" wide on top. This tube fitted exactly into 1/16" guides on the inside of the outer cylinder thereby being prevented from striking the liner on the introduction of the funnel into the bomb.

2.5 Topping of Charge and Closing of Bomb. The filled bomb was lifted from the charging pit by the monorail hoist. A covering of lime was placed above the charge to complete the inert liner which prevented the reaction of the charge with the bomb. This covering was very necessary as attack of the bomb or flange at the top due to defective liner resulted either in contamination of the product with iron or even in a "burn-out" through the bomb or flange which destroyed the bomb and permitted all or much of the charge to be blown out of the bomb and thus wasted. The "topping" was performed as follows: The charge was smoothed and compacted by pressing with a cylindrical wooden paddle or mold of diameter equal to inside diameter of liner. Lime was then poured on top of the smooth surface of the charge and compacted with a form similar to the above but of 6" diameter until level with the top of the flange. The cavity in the plug of the top flange was filled with lime by jolting. The top flange was then bolted in position.

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A triangular handle or bail for lifting the bomb was inserted through two opposite bolt holes of the flange and secured by nuts. The bomb was then placed in the furnace by means of a chain hoist which was supported on a monorail running above the loading line, over the furnace and cooling spray and into the opening room.

2.6 Preheating and Ignition of Charge. The preheating furnace was a gas-heated soaking pit approximately 3' wide by 3½' deep by 12' long. The pit was lined with ordinary commercial fire brick and covered with six removable covers built of magnesia brick held between 1/4" sheet steel plates bound around the edges by welded sheet and supported on a frame work of angle iron. A hole through the center of each cover permitted the introduction and removal of bombs.

The soaking pit was heated by a low-pressure natural gas-air mixture burned in Burdett Radiant Heat Gas Burners produced by the Burdett Manufacturing Company, Chicago, Illinois. The mixing and proportioning equipment was designed and supplied by the Burdett Company. Twenty-four #25 Type A Burdett Burners with a rated capacity of 10,000 BTU per hour each were arranged evenly at the bottom of the pit along the two sides. Temperatures were measured by metal-shielded chromel-alumel thermocouples arranged along the sides and in the top and bottom of the furnace. When the furnace was at equilibrium, the temperature throughout the central portions where the bombs were placed was very even, being 40-50° hotter near the top of the furnace.

Six 6" bombs could be placed in the furnace at a time during normal operation. They were lined up in the center lengthwise of the furnace between two rows of burners. The timing of the introduction and removal of the bombs was fairly important in that introducing too many or removing too many at a time disturbed the furnace temperature sufficiently that it was found best to stagger the introduction of the bombs at proper intervals (every 5 minutes or more) to maintain sufficiently even heating.

The proper length of preheat (called "firing time" below) and the temperature of the preheating furnace varied with such a number of factors that the specification of temperature and firing time for general operation is not advisable. However, for most of the products used during

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the major part of the operation a temperature of 650°C (1200°F) was used giving a firing time of 47 to 55 minutes. The relation of firing time, furnace temperature and reactants will be discussed below.

After the reaction had occurred, 45 to 60 minutes after placing the bomb in the furnace, it was removed by the chain hoist to a cooling spray of water arranged in line with the furnace. After several hours the bomb and its contents were sufficiently cool to handle and to expose to the air.

2.7 Handling of Slag. The bomb was removed from the cooling spray to a room equipped with a pit in the floor covered with grating made of 1/4" steel bars separated by 1/4" spaces. The pit was vented from the bottom by ducts leading to the main exhaust fan of the building. In emptying the bomb the cover was removed from the bomb, the side wall chipped down by a pneumatic chisel similar to a concrete chipper, the loose wall material dumped on the grating. The bomb was placed mouth downward on a pneumatic jolter and jolted until the ingot of metal was loosened and fell to the floor. Remaining wall or liner material was chiseled loose and all liner material and slag were swept onto the grating which acted as a sieve permitting the 1/4" and finer material to pass into the barrel or drum below the screen. This product consisted chiefly of liner material, CaO or MgO, poor in both fluorine and uranium. Larger pieces, including most of the slag or MgF_2, were removed to a chute in the cover of an adjacent pit and dropped into a second container. This product contained most of the unrecovered uranium. These two classes of residue were reserved for recovery of uranium values and of fluorine as HF elsewhere.

2.8 Treatment of Ingot or Biscuit Metal. The ingot of metal or "biscuit" was chipped clean of adhering slag and oxide and was now ready for remelting and casting. The "biscuits" from the 6" bomb were 4 7/8" to 5 1/8" in diameter and 3 1/4" to 3 1/2" high, weighing 40 to 42 pounds. When well separated from slag they were cylindrical with smooth sides and flat, slightly wavy top surfaces. Under favorable conditions described in succeeding sections of this report slag covered tops and rough sides with protruding fins were sometimes obtained.

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While the major portion of the metal produced at Iowa State College was reduced in 6" bombs 36" long, considerable metal was also produced toward the close of the production period in 10" bombs 40" long. Some experimental work was done in bombs up to 14" in diameter.

The construction of the bomb and the lining, as well as the loading and firing processes were the same for the 10" bomb as for the 6" except for wall thickness. The 10" bomb was made of standard 10" pipe, 10.125" i.d., 40" long. The mandrel used with this bomb had a diameter at top of 9" tapered to 8 3/4" at bottom. Thus the refractory liner wall was 9/16" thick at the top tapering to 11/16" thick near the bottom. The standard charge of UF_4 at Iowa State College in the 10" bomb was 168 lbs. which produced a theoretical yield of 127.5 lbs. During the period from Sept. 18, 1944 to Nov. 9, 1944, numerous reductions were made in 10" bombs with usual yields of 122 to 126 lbs. or yields of 95 to 99 per cent with an average yield of 97.6 per cent over a series of 162 consecutive reductions.

3. Production, Processing and Specifications of UF_4

The properties of the UF_4 used in the reduction process had much to do with the economy of operation particularly with the yield obtained in the reduction to metal. Particle size, density and the presence of oxygen compounds had a great influence on the reactivity of the salt and on the yield of metal obtained. The purity of the metal was, of course, limited approximately to the purity of the salt. Therefore, its correct manufacture from raw material was very important in the production of metal.

3.1 Manufacture. The UF_4 was manufactured by the hydrofluorination of UO_2 by dry HF at 550°C at atmospheric pressure. The dioxide was obtained by the reduction with H_2 of U_3O_8 from the thermal decomposition of uranyl nitrate. The nitrate had been purified of rare earths and other forbidden contaminating elements by an ether extraction.

Practice differed somewhat at various plants but in general the procedure involved the following essential steps and conditions: The UO_2 from the H_2 reduction of U_3O_8 was packed in graphite trays stacked in series. One plant used magnesium trays heated in cylindrical furnaces

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arranged in tandem. The graphite trays were introduced into gas-heated furnaces and maintained at 550°C for about 8 hours. The HF gas at atmospheric pressure was passed over the surface of the oxide layer in successive trays in the stack, the excess carrying with it as it passed the trays the water formed in the reaction. In earlier production the trays were cooled under streams of N_2 or CO_2 to remove excess HF although later they were permitted to cool in air without apparent ill effect. After cooling the salt was ground to specifications.

3.2 Processing at Plant. The UF_4 was removed from the hydrofluorination trays in lumps which were sometimes quite hard. Since it was found that not more than 10 per cent of the salt should be +100 mesh, it was necessary to grind it before use. The tetrafluoride was ground in a Model LG-2 Williams Mill of the swing hammer type built by the Williams Patent-Crusher and Pulverizer Co., St. Louis, Missouri, driven by a 220 v. 3 ph..10 h.p. motor and equipped with an air lift system which collected the salt in a cyclone settler and separated the very fine dust in a bag filter system. The grating bars of the mill were replaced by a screen of sheet metal perforated with 1/64" holes. The grind produced by this arrangement lay between the following limits:

Sieve No.	Per cent Passed		
	Lower limit	Upper limit	Typical
60	96%	98%	96.6%
80	92	94	92.6
100	87	91	89.2
200	70	78	73.2
325	45%	55%	51.2%

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Salts received ready for use from the Mallinckrodt Chemical Works ground in a Mikropulverizer usually had the following size distribution:

Sieve No.	Per cent Passed	
	Lower limit	Upper limit
60	98%	—
80	94	96%
100	90	92
200	70	75
325	52	60

3.3 Effect of Particle Size of UF_4 on Yield. Salts having distributions between any of the above limits gave equally good reduction results. No study was made of the effect on yield of sizes within narrow limits, since the grinding always produced a wide distribution between 100 mesh and at least 40 per cent -325 mesh, varying not only with the method of milling but with the properties of the oxide from which the fluoride was prepared. It was not deemed advisable to separate by screening the large amount of salt necessary for an exhaustive study of the effects of size within narrow limits. However, inadequate grinding at the beginning of production led to failures.[8] The use of some materials, which were received coarsely ground, established the following upper limits of particle size as definitely deleterious to yield.

Sieve No.		Per Cent Passed
60	.....	96%
80	.....	91
100	.....	80
200	.....	54
325	.....	40

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Yields of 85 to 90 per cent of poorly separated, slag-encrusted metal were obtained with this product (normal yield at the time was 92 per cent). Thus it appeared that as much as 10 per cent of +80 mesh or 20 per cent of +100 mesh lowered the yield by 2 to 7 per cent. There was usually not more than half that amount of either of these sizes.

The lower limit of size was also roughly established by the behavior of the material collected in the filter bags of the Williams Mill. Sieve analyses showed this material to be all -325 mesh. This product gave a yield of 77.6 per cent metal, poorly separated and slag covered.(9) The actual size of this -325 mesh material was not determined.

3.4 Effect of Density of UF_4 on Yield. Attempts were also made at the beginning of the project to prepare UF_4 by wet-way reactions. The product was precipitated, filtered in filter press and dried. It emerged from the pressing and drying processes in light flakes. The result was a packing density of only one-third to one-half that of the usual dry-way product. The reduction of this product with Mg was not investigated but it was reducible to massive metal with Ca only by pressing the charge as described in the previous report on production by Ca.(1,10) In both cases lower yields of metal of poor quality were obtained; dry-way materials of high density which met other requirements, i.e. assay etc., produced yields up to 97 per cent. The deleterious effect of low density was due to both low heat conductivity resulting in lack of adequate heat input during preheating and to the low concentration of charge and consequently to the low concentration of heat of reaction resulting in failure to reach a sufficiently high temperature to fuse the products. Salts with packing density of less than 3 g/cc were found to give poor yields. The packing density of standard UF_4 received varied from 3.3 to 3.6 g/cc. The packing density of the mixed charge in the bomb varied from 2.6 to 2.75 g/cc.(11)

3.5 Effect of UO_2 and UO_2F_2 on Yield. In the early production of UF_4 various lots of salt produced very low yields or even failed to react at all. On analysis these lots were frequently found to be high in either UO_2 (ammonium oxalate insoluble) or UO_2F_2 (water soluble) or both. During the hydrofluorination process incompleteness of treatment left a residue of UO_2, or the presence of water in the HF resulted in the formation of

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UO_2 by hydrolysis, or the production of U_3O_8 or UO_2F_2 by oxidation at higher temperatures. The admission of air into the hot chamber during the reaction or during the cooling period would also have produced U_3O_8 or UO_2F_2.

In any case UO_2 or UO_2F_2 were both frequently found to be present in poorly reacting lots of UF_4 which were within specifications with regard to density and particle size. In an effort to determine exactly the permissible limits of UO_2 a series of blends were prepared, analyzed and reduced. Five lots containing 0.75 per cent, 1.56 per cent, 2.92 per cent, 8.23 per cent and 11.44 per cent respectively of insoluble oxide were used. These lots were reduced with 7.5 per cent excess Mg in the regular production processes and each lot was cast separately. The over-all yield of cast metal was determined as shown in Table 1.

Table 1

EFFECT OF UO_2 IN UF_4 ON YIELD OF U

Lot No.	UO_2 (Ammon. Oxal. Insol.)	Crude Yield	Casting Yield	Over-all Yield
530	0.75%	90.6%	93.0%	85.0%
534	1.56	90.4	92.6	83.6
531	2.92	88.9	93.2	82.8
535	8.23	73.5	80.2	58.9
533	11.44%	71.6%	67.1%	48.0%

It will be seen that the cast yields of the first three lots were practically the same, but the crude yields dropped slightly with increasing dioxide. The over-all yields dropped by 1.4 per cent and 2.2 per cent. It may be concluded that 3 per cent of oxide produces approximately a 2 per cent decrease in yield and should not be tolerated. The 8 per cent dioxide content caused a decrease in both the crude and in the cast steps and an over-all decrease of 25 per cent, while the 11 per cent content caused an over-all decrease of 37 per cent.

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The effect of UO_2F_2 was studied with Lot L 2717 VR01 of UF_4 which failed to react on heating with Mg.[8] No significant amount of dioxide was found but analysis revealed the presence of 15.8 per cent of UO_2F_2 (water soluble fraction). Assay for UF_4 revealed only 82.6 per cent, the remainder being carbon from the trays and silica. Further lots containing 3.20 per cent of UO_2F_2 reacted but gave biscuit yields as low as 86 per cent (90-94 per cent yield normal at the time). Thus it appeared that 3 per cent of UO_2F_2 was quite detrimental and 15 per cent even prevented reaction. On the basis of these and subsequent operational observations 3 per cent of combined UO_2 and UO_2F_2 was set as the permissible limit, or an assay of 97 per cent UF_4 was adopted as the composition specification.

3.6 Purity of UF_4. The purity of the UF_4 was controlled very rigorously during the production period. Graphite from the trays and high iron occurred in some of the early lots. After production was standardized, however, purity became very consistent. Typical Mallinckrodt Chemical Works salt ran from 12 to 18 ppm in Fe, 0.15 to 0.83 per cent UO_2, 0.83 to 1.28 per cent UO_2F_2. Boron content was well below 0.2 ppm but was analyzed routinely only within this limit. Thief samples of UF_4 were taken at Ames from those supplies which required grinding for check on iron pick-up.

3.7 Specifications. The final specifications adopted for UF_4 were:

Grind: not over 6% +80, not over 12% +100, not over 70% -325 mesh.

Assay: 97% UF_4

Purity:		
	Fe	50 ppm
	Mn	25 ppm
	B	< 0.2 ppm

4. Processing and Specifications of Magnesium

The magnesium used in production has been obtained for most part from the New England Lime Company, Canaan, Connecticut and was produced by the reduction of dolomitic oxide by ferrosilicon. The volatile metal

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was condensed in iron sleeves into muffs about 10" in diameter and 8 to 12" long. These muffs consisted of 1 to 1 1/2" of dense metal forming an outer shell from which fingers or asparagus-like structures or fibers and platelets extended inward leaving an opening about 4" in diameter in the center.

4.1 Processing of Mg at Plant. It was necessary to reduce these aggregates to 10 to 50 mesh metal.(13) It was first necessary to break down the muffs to sizes that could be introduced into the primary cutter. This was done by crushing the muff in a large punch press equipped with cutting edges on the spindle and table. The resulting pieces, 4 or 5" long by 2" wide by 1" thick could be fed into the next cutter. This product was passed over an Automatic Spout-Type Magnet supplied by the Dings Magnetic Separator Company, Milwaukee, Wisconsin, to remove any tramp iron contained in the original material or acquired in the first breaking up, both to protect the following cutters and to prevent contamination of the product by iron.

The broken-up, magnetically cleaned magnesium was next reduced by cutting in a Type AB Hog, Serial No. C-5970 built by Mitts and Merrill, Ind., Saginaw, Michigan. This mill consisted of 8 knives mounted in a large rotor cutting against breaker bars mounted in the housing. Equipped with a screen of 1/2" steel plate perforated with 1/4" holes this mill reduced the magnesium to pellets 1/4" in diameter and smaller. Its capacity was 200 lbs/hr of lump Mg or more if finer material was introduced.

The magnesium from the above mill was again passed over the magnetic separator and introduced into the next cutter, a Type 2-SB Rotary Knife Cutter built by Sprout-Waldron and Co., Muncy, Pa. This cutter was equipped with 5 rotary and 5 stationary blades 24" long with laid tool steel cutting edges, driven by a 220 v, 3 ph., 15 h.p. motor. This mill had a capacity of 125 lbs/hr of Mg from the hog.

The cut metal was then passed over a 50 mesh mechanical screen for the removal of fine Mg and MgO knocked from the surface of the metal during cutting. These screenings were removed because of the deleterious

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effect of the oxide on the reaction yield and because most of the impurities in the Mg, particularly of the B and Fe, were removed with them.

The screened Mg was passed over the magnet again just prior to weighing and mixing in the charge.

4.2 Effect of Mg Produced by Different Processes on Yield of U.

Magnesium produced by various processes was tried out during the development of the process. The first obtained was electrolytic Mg, distilled for purification. It was comparable to the ferrosilicon metal used later and since it involved a separate step of distillation, only a small amount of it was produced to get the work started. Mg produced by the Pidgeon process by reduction of dolomitic oxide by ferrosilicon was next obtained, supplied by the New England Lime Co., Canaan, Conn. Metal by the same process was obtained from other producers and finally some metal by the carbothermic reduction produced by Permanente.

A number of studies were conducted to determine the effect on the yield of uranium of these types of Mg produced by different methods. Some types were quite consistent in their behavior while others varied greatly. Sufficient stocks of each type (enough for at least 12 reductions under any given set of conditions) were procured in order that variations at the source should not enter into the results and they were processed under identical conditions as described above. The ground material resulting from the various types, however, was not the same in size or shape due to differences in structure of the different types. Thus the New England Lime Company crowns produced fibrous material while the Permanente dense crystals produced quite granular particles, resulting in a difference in the surface to mass ratio. These differences are reflected in the sieve analyses of the products. Separate studies at different times produced varying results for a given type of Mg due to other variables, such as fluoride or liner material. However it is possible to compensate somewhat for these variables by comparing regular production results at those times. The results of two such studies are summarized here.

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In the first study[14] various types of Mg were obtained from the Permanente Metals Corporation, Permanente, California, from the New England Lime Company, Canaan, Conn., and from Magnesium Reduction Company, Luckey, Ohio.

4.2.1 Characteristics of Mg of Different Types from Various Sources. The various types of Mg from the different sources had the following characteristics:[15]

I. Permanente Metals Corporation, dense, "popcorn". A relatively symmetrical crystal, approximately equi-axial, 3 to 6 mm along its edges, in clusters like popcorn balls. Each crystal was very hard and dense and difficult to cut in the mills. The final product after cutting in the Sprout-Waldron Cutter with blades set at 0.030" (all samples described below were cut at this setting) consisted of small, symmetrical cubicles with smooth faces. The sieve analysis is shown in Table 3. As will be seen the particles of the Permanente products were much more uniform than the other types, larger on the average and contained less fines.

II. Permanente, "fibrous" or "foamy". This material consisted of smaller crystals (1 to 3 mm) than the above with fine fibers occupying the interstices. Superficially the unit particles appeared to be different, but actually they were of the same symmetrical crystalline type and after milling the final product was very similar to Type I in particle size, shape and nature of surface. There is very little essential difference in the two forms, if any.

VII. Permanente ground through Williams Hammer Mill in St. Louis, Mo. for preliminary cutting. Final grind in Sprout-Waldron Cutter at Ames. Results, similar to above. About 20 per cent of the material from the hammer mill was too coarse for the Sprout-Waldron Cutter. This situation might be remedied by the use of a finer screen or less clearance in the breaker bars of the hammer mill.

III. New England Lime Company No. 2 Crystals. These "crystals" consisted of fibrous dendritic structures arranged in parallel aggregates forming long "fingers". These "fingers" ranged from one-half to several inches long and one quarter to one inch in diameter. On cutting they produced elongated flat units rather than symmetrical particles. They produced much more fines than did the Permanente product.

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IV. New England Lime Company, regular stock, consisted of crystals and broken crowns and muffs. It was very little different from the above after grinding because the crowns and muffs simply consisted of parallel "fingers" embedded in a nearly fused base formed on the sides of the condenser. The latter produced more symmetrical particles.

VI. New England Lime Company; preliminary cut in hammer mill, final cut in Sprout-Waldron Cutter. It was similar to the above New England products.

V. Magnesium Reduction Company Crowns. The Magnesium Reduction Co. crowns were similar to those of New England Lime Co. but the dendritic fibers were much finer. The final product consisted largely of elongated fibers, much finer than those of the New England Lime Co. fibers and contained much more fines.

VIII. Magnesium Reduction Company Crowns; screened. In order to get our Magnesium Reduction Co. product more nearly equivalent to that of the New England Lime Co. size distribution some of the Type V material was screened over 18 mesh mechanical screen and the 10 to 18 fraction which still contained much fine material (see sieve analysis) was used. However, the size distribution was still quite different from that of the New England Lime Co. It was not possible to cut the Magnesium Reduction Co. magnesium to the same distribution as that of the New England Lime Co. because of the fineness of its component fibers.

The sieve analyses of the various types of magnesium are given in Table 2.

4.2.2 Procedure of Experiment.[16] In this experiment a number of series were run consisting of 12 to 24 reductions or shots of each type of Mg under fixed conditions with all other materials kept constant. The various types of Mg were alternated successively in the mixing of the charges. In this way fluctuations in furnace behavior, changes of operators in the production line with change of shifts and other human and mechanical variables were as nearly as possible balanced out.

Bomb linings were made of Ste. Genevieve hard-burned lime mixed with 4 per cent magnesium powder, 50 to 80 mesh, to within 10" of the top of the bomb, finished and topped with Kelly Island Lime and Transport Company's dolomitic lime without magnesium fines. Series of 12 shots of

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each type of Mg were also run at various furnace temperatures from 1050°F (575°C) to 1300°F (705°C) by 50° (F) intervals. The crude ingots or "biscuits" of each type were cast separately and reduction of "biscuit" yields and casting yields were recorded for each run. The over-all yield or product of reduction yield times casting yield is necessary since the crude metal weight with slag inclusions and incrustations represents a false yield.

TABLE 2

SCREEN ANALYSES OF TYPES OF Mg USED
IN Mg COMPARISON STUDY NO. 1

Type Mg	Size Range					
	+10	10-20	20-30	30-40	40-60	-60
I	1%	68%	18%	8%	3%	2%
II	1	79	12	4	1	3
III	1	53	25	4	7	0
IV	1	38	27	19	13	2
V	1	29	24	21	18	7
VI	1	46	28	16	8	1
VII	1	67	21	9	1	1
VIII	1%	35%	31%	22%	10%	1%

4.2.3 Results of Investigation.[17] The biscuit casting and over-all yields of the various types of magnesium at each furnace temperature are presented in Table 3 and shown graphically in Figures 2 and 3.

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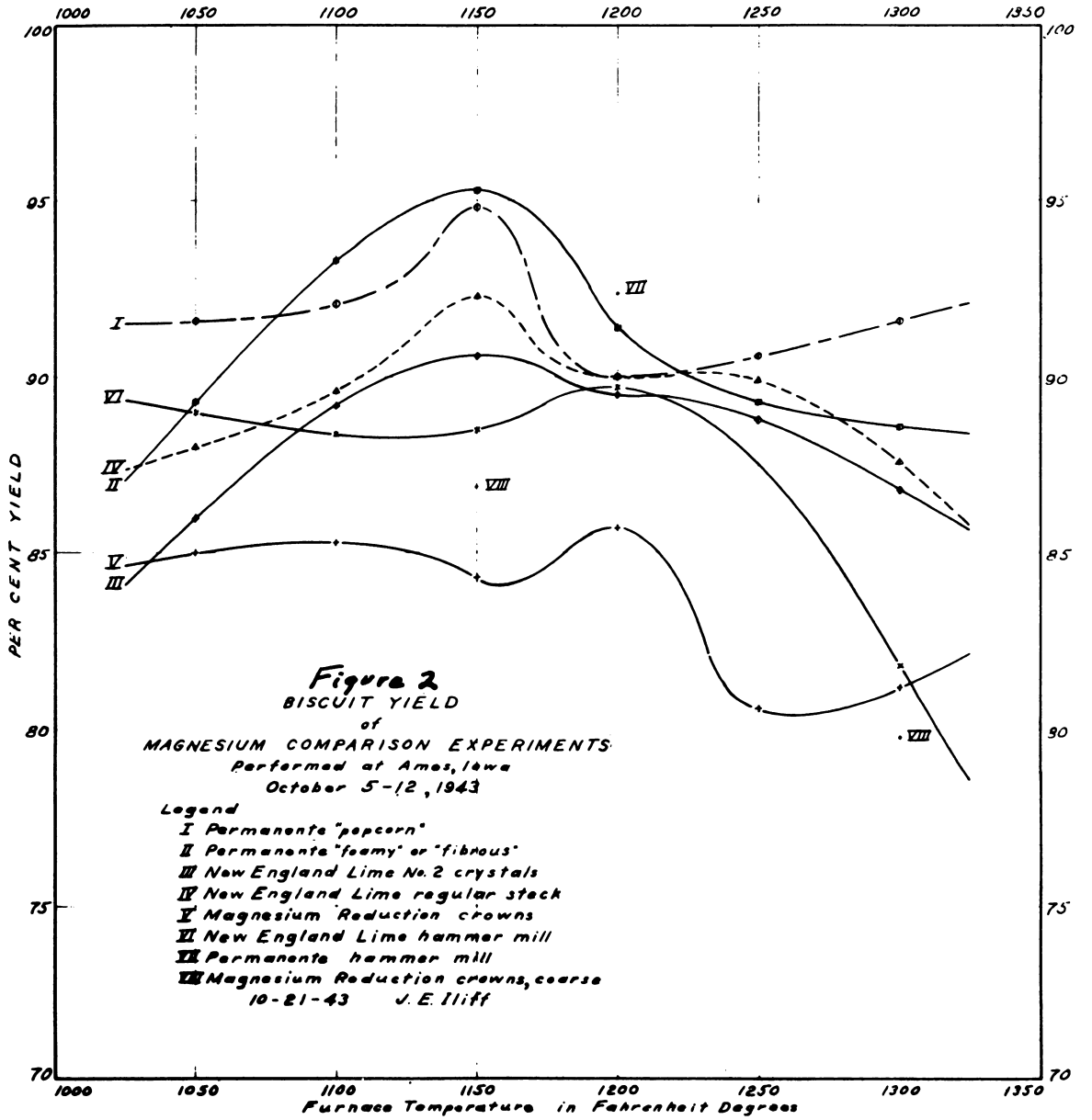

Figure 2
BISCUIT YIELD
of
MAGNESIUM COMPARISON EXPERIMENTS
Performed at Ames, Iowa
October 5-12, 1943

Legend
I Permanente "popcorn"
II Permanente "foamy" or "fibrous"
III New England Lime No. 2 crystals
IV New England Lime regular stock
V Magnesium Reduction crowns
VI New England Lime hammer mill
VII Permanente hammer mill
VIII Magnesium Reduction crowns, coarse
10-21-43 J. E. Iliff

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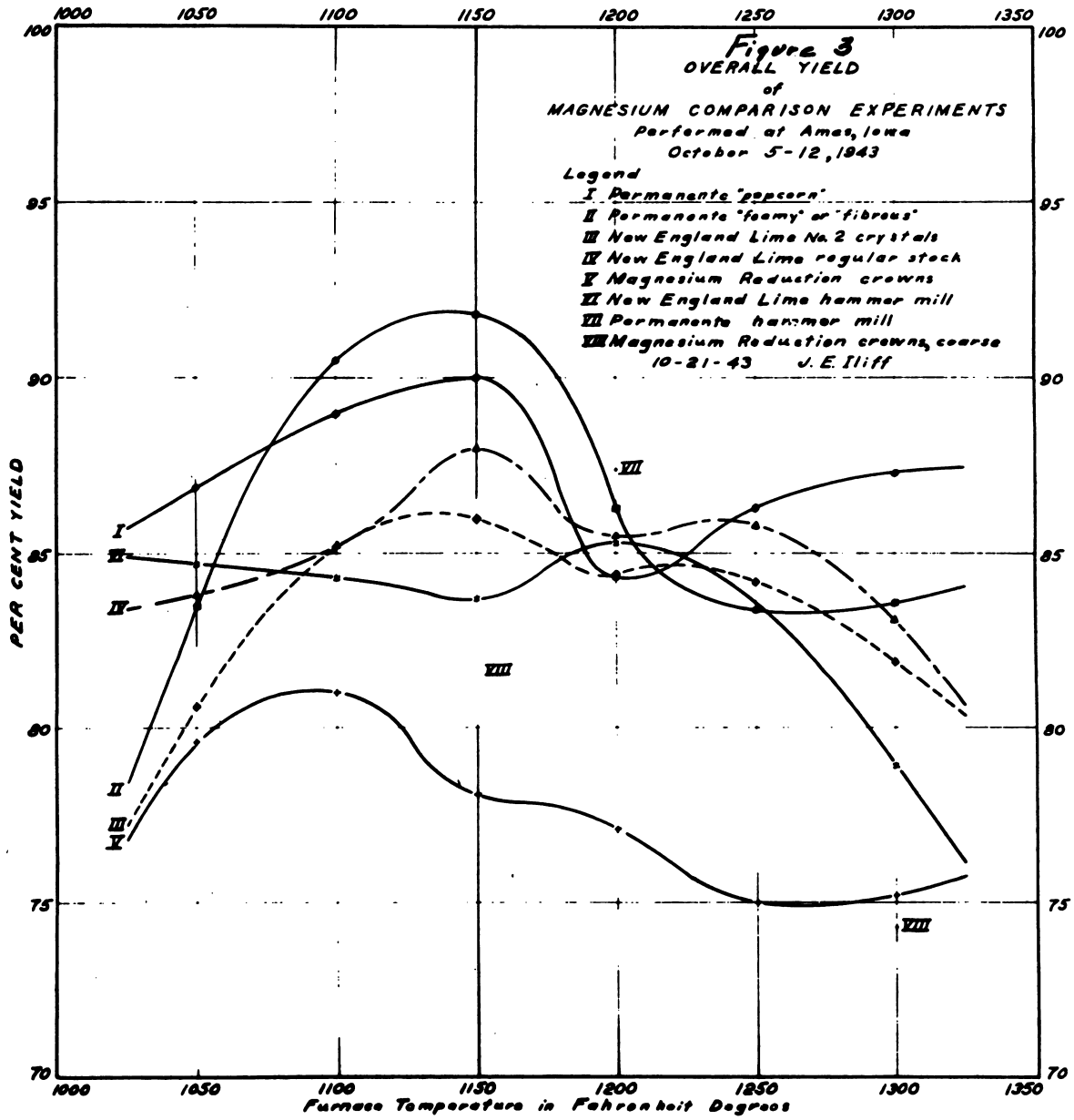

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TABLE 3

EFFECT OF VARIOUS TYPE OF MAGNESIUM ON YIELD OF URANIUM[18]

Type Mg	Stage of Yield	Furnace Temperatures 1050°F 575°C	1100°F 600°C	1150°F 625°C	1200°F 650°C	1250°F 675°C	1300°F 705°C
I. Permanente (Dense, popcorn)	Biscuit	91.6%	92.1%	94.8%	90.0%	90.6%	91.6%
	Casting	94.9	96.7	94.9	93.6	95.2	95.4
	Over-all	86.9	89.0	90.0	84.3	86.3	87.3
II. Permanente (Fibrous, foamy)	Biscuit	89.3	93.3	95.3	91.4	89.3	88.6
	Casting	93.6	97.0	96.4	94.4	93.4	94.4
	Over-all	83.5	90.5	91.8	86.3	83.4	83.6
VII. Permanente Hammer Mill	Biscuit	----	----	----	92.4	----	----
	Casting	----	----	----	95.5	----	----
	Over-all	----	----	----	87.4	----	----
III. New Eng. Lime No. 2 crystal	Biscuit	86.0	89.2	90.6	89.5	88.8	86.8
	Casting	93.8	95.5	95.0	94.3	94.8	94.4
	Over-all	80.6	85.2	86.0	84.4	84.2	81.9
IV. New Eng. Lime Regular Stock	Biscuit	88.0	89.6	92.3	90.0	89.9	87.6
	Casting	95.3	95.1	95.3	94.9	95.5	94.9
	Over-all	83.8	85.2	88.0	85.5	85.8	83.1
VI. New Eng. Lime Hammer Mill	Biscuit	89.0	88.4	88.5	89.7	----	82.8
	Casting	95.3	95.4	94.6	95.1	----	95.4
	Over-all	84.7	84.3	83.7	85.3	----	78.9
V. Magnesium Reduction Co. Crowns	Biscuit	85.0	85.3	84.3	85.7	80.6	81.2
	Casting	93.7	95.1	92.6	90.0	93.1	92.6
	Over-all	79.6%	81.0%	78.1	77.1%	75.0%	75.2
VIII. Magnesium Reduction Co. Crowns, Screened	Biscuit	----	----	86.9	----	----	79.8
	Casting	----	----	94.0	----	----	93.0
	Over-all	----	----	81.7%	----	----	74.3%

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The yield curves show that the various types of Permanente magnesium produced the highest yields and that of the Mangnesium Reduction Co. produced the lowest yields while the New England Lime Company materials produced intermediate values. Secondly, it appeared that each type had an optimum preheating temperature. However, the optima for some of the types did not occur in this experiment at the same temperatures as had been previously observed for those types. This difference will be discussed below.

It was also very clearly demonstrated in this experiment that the over-all yield, not merely the biscuit or reduction yield, must be determined in comparing production data. This was shown most strikingly in the case of Type V, Magnesium Reduction Co. crowns. Here the maximum in biscuit production occurred at 1200°F whereas in our previous experience it had occurred at 1100°F. Also a minimum occurred at 1150°F at which temperature all other types produced maxima. These inflections appeared to be without reason. But when the crude metal had been cast and the over-all yields calculated and plotted, the maximum at 1200°F disappeared and the true maximum at 1100°F appeared, confirming our previous experience with Magnesium Reduction Co. magnesium. The apparently high biscuit yield was due to poor separation of metal and slag and included considerable slag. Such biscuits always produced lower casting yields. In this connection it may be seen that a graph of casting yields against biscuit yields (Fig. 4) shows about 0.25% decrease in casting yield per 1.00 per cent decrease in biscuit yields. Such extreme cases as the 1200°F point on Type V curve deviate greatly from this relation, however.

The major object of the best was to compare the productivity of the various types of magnesium. The results in this regard were quite clear. The various types of Permanente magnesium were outstandingly superior at 1100° to 1150°F and at higher temperatures at 1300°F. The latter observation was in keeping with the experiences of the Mallinckrodt Chemical Works. At 1200°F to 1250°F, however, the Permanente and the New England

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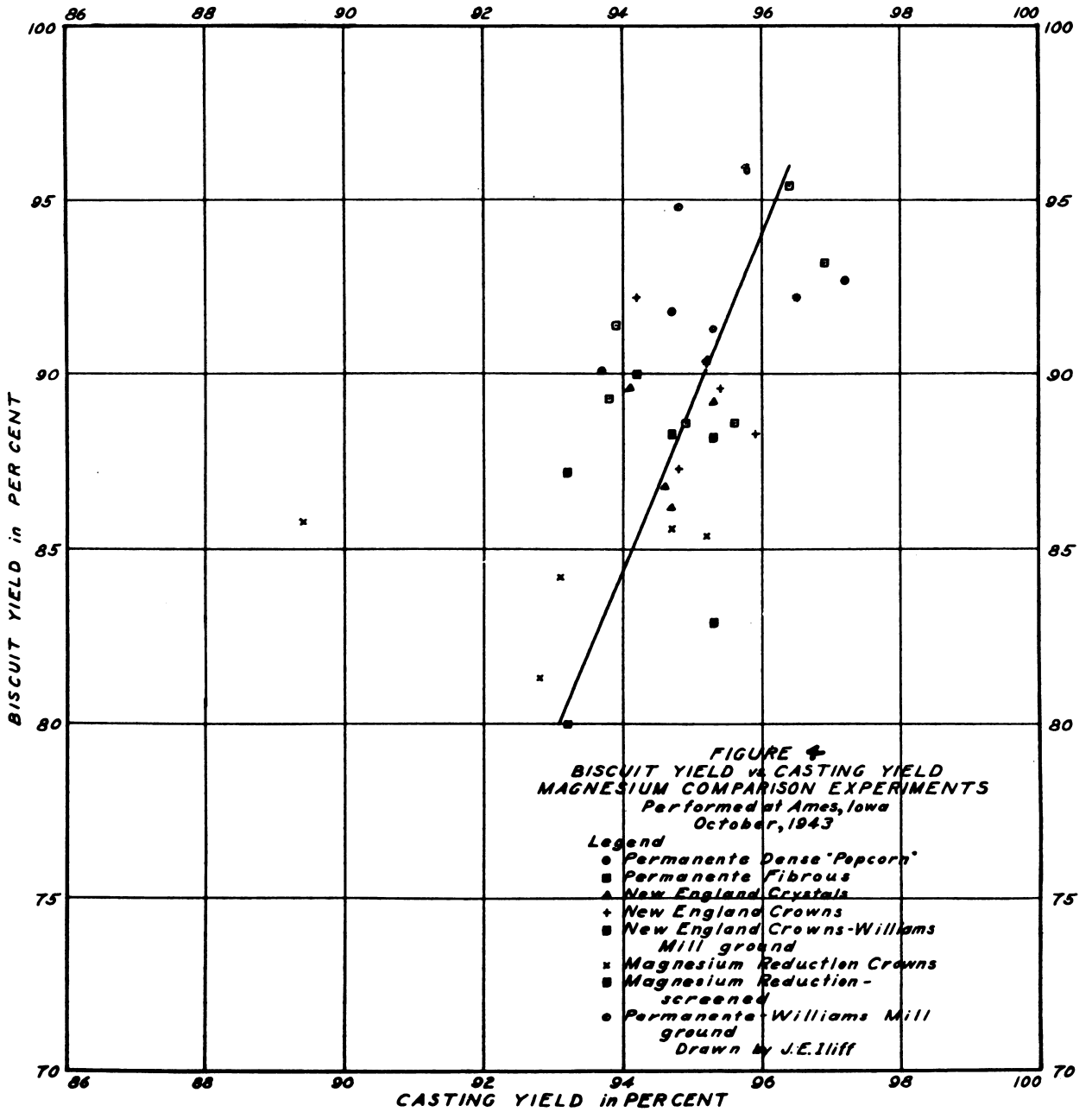

FIGURE 4
BISCUIT YIELD vs CASTING YIELD
MAGNESIUM COMPARISON EXPERIMENTS
Performed at Ames, Iowa
October, 1943

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Lime Co..products behaved very similarly. At the average of their maxima the Permanente types exceed the New England Lime Co. types in over-all yield by 5 per cent. These results were not substantiated in the next tests (Section). Throughout the range investigated, the Magnesium Reduction Co. crowns are 3 to 14 percent below the other products except at one point.

4.2.4 Conclusions.[19] The explanation of these differences was not at all obvious. All of these products were so pure chemically that the concept of greater activity due to calcium or other contaminants even as a catalyst seems untenable. Difference of crystal systems had been suggested but Dr. Rundle of Iowa State College found X-ray evidence of only one crystal system in all the types. The only apparent differences were (1) the particle size distribution; (2) particle shapes and (3) surface condition. Less obvious differences were content of active metal or of oxygen and nitrogen.

It will be seen that the Permanente materials had the greater percentages of larger particle sizes while the Magnesium Reduction Co. crowns which produce the lowest yield had the highest content of fines. Also, it will be observed that Type VIII which was the Type V, Magnesium Reduction Co. crowns, passed over a 20 mesh screen, showed an increase of over-all yield of 3.5 per cent over the Type V before screening. Not all -20 material was removed, but the composition approached that of the New England Lime Co. product. That these variations in size might be the source of difference in yield necessitated a study of the effect of particle size, described in the next section of this report.

The nature of the surface varied considerably, the Permanente offering a bright, freshly cut surface while many of the Mangesium Reduction Co. particles consisted of original needle-like crystals with the surfaces formed at the time of condensation. The latter surfaces might have been expected to be corroded and hence to delay reaction. That this was not true was indicated by the fact that the Magnesium Reduction Co. product reacted more quickly than either of the others.

Another significant difference in the performance of the various types of magnesium at the various temperatures was the firing time.

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An optimum firing time was observed for each type of magnesium. Sixty minutes of preheating produced maximum results with Permanente, 48 to 53 minutes with different types of New England Lime Co. and 47 minutes with Magnesium Reduction Co. It is obvious that insufficient heating or too quick firing would produce poor results by failure to add the necessary amount of heat. The decrease of yield by too long heating was not due to the addition of too much heat, however, as was shown by occasional good yields obtained on heating to two hours or more, but to the hydrolysis of the tetrafluoride by water in the lining refractory.

Hence, the optimum time of preheating was a proper balance between the longer time for the introduction of sufficient heat and the shorter time to prevent side reactions. At too high preheating temperatures the charge near the wall reached ignition temperature before sufficient heat had been added and a low yield due to the addition of insufficient heat resulted.

4.2.5. Supplementary Experiment. In the second experiment[20] some of the same forms of New England Lime Company magnesium were used along with two new ones, the fine or No. 5 crystals and the "heads" from the condenser and some broken crowns and crystals from the Amco Magnesium Company, Wingdale, N. Y. The products had the following characteristics:[21]

(a) New England Lime Company Muffs - These "muffs" were received in more or less hollow cylinders about 10" in diameter. The bottom and sides were composed of a layer of nearly fused magnesium approximately one inch thick which formed on the sides of the condenser. The center part of the "muff" consisted of parallel "fingers" embedded in the semi-fused base.

(b) New England Lime Company No. 2A Crystals - These "crystals" consisted of fibrous dendritic structures arranged in parallel aggregates forming long "fingers". These "fingers" ranged from one-half to several inches long and one-quarter to one inch in diameter. On cutting they produced elongated flat units rather than symmetrical particles.

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(c) New England Lime Company No. 5 A Crystals - This material consisted of smaller crystals than the No. 2A. The crystals resembled common rock salt. There was a large amount of foreign material present and this type was used only after sorting by hand.

(d) New England Lime Company "heads" or "pie plates" - These "pie plates", formed at the ends of the condenser, consisted of a nearly fused base with parallel "fingers" embedded and extending upward from the base. After cutting the "pie plates" with a punch press, there was very little essential difference between these "pie plates" and the "muffs".

(e) New England Lime Company Muffs ground in large Hammer Mill - This product was received ground, having been put through the Williams swing-type hammer mill at Canaan, Conn. All but a small fraction (0.25-0.5%) of this material passed through a 1/4" screen and could be fed directly into the Sprout-Waldron Mill. The residue consisted of compact solid oval pellets 1/4" to 1/2" in the various diameters. However, these pellets were large for direct cutting in the Sprout-Waldron.

(f) Amco Magnesium Company, Crystals and Broken Crowns - This material consisted of a mixture of broken crowns and "fingers" similar to New England Lime Co. broken muffs and No. 2 crystals. The crowns were received cut into 3" to 4" pieces.

After grinding there was no essential difference between the various New England Lime Co. products except the fine crystals. These had more exposed surface and higher surface contamination. The Amco product was quite similar to the corresponding New England Lime Co. product.

This experiment was conducted with Mallinckrodt Chemical Co. tetrafluoride, Mg in 7 1/2 per cent excess, a bomb liner of Ste. Genevieve lime with 3 per cent Mg fines in the bottom section of the bomb, 1 per cent Mg fines in the side wall and Kelley Island dolomitic lime in the top. The furnace temperature was 1200°F.

The yields produced by the various types of Mg used in this study are summarized in Table 4.

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TABLE 4

FURTHER STUDY OF EFFECT OF VARIOUS TYPES OF Mg ON YIELD OF URANIUM(22)

Type Mg					
Design in Prev. Study	Design in This Study	Description	Biscuit Yield	Casting Yield	Over-all Yield
IV	a	New Eng. Lime Muffs	97.2%	95.9%	93.2%
IV	b	N. E. Lime Heads, "pie plates"	98.3	93.8*	92.2*
III	c	N. E. Lime 2A Crystals (med.)	98.0	94.5	92.6
	d	N. E. Lime 5A Crystals (fine)	98.1	93.8	92.0
	e	N. E. Lime Williams Mill	97.2	95.1	92.4
	f	Amco Magnesium Co. crystals & crowns	96.3%	95.9%	92.4%

*Excluding one faulty casting, not due to materials being tested.

It will be observed that under regular operating conditions variations of yield were very small and the yields may therefore be considered as representatives of the types of Mg employed. It is particularly noticeable that the New England Lime Co. muffs on the basis of consistency which in performance and composition had already been adopted as the regular Mg for production gave an over-all yield of 93.2 per cent in this experiment as compared with an over-all yield of 85.5 per cent in the earlier experiment. This difference was probably due more to improvement of liner material and liner installation and possibly of tetrafluoride than to differences in the magnesium. Hence, these two results may be used in correlating other portions of the two experiments.

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On the basis of these experiments and of other smaller studies the muffs produced by the New England Lime Co. were adopted as standard product for the process. In consistency of behavior and of composition and purity, this product was most dependable. The high results shown by the Permanente carbothermic product in the first study were not substantiated in other tests and its behavior was very erratic.

4.3 Effect of Particle Size of Mg on Yield of U.[23] In the attempt to set up specifications for particle size of Mg for use in the reduction of UF_4 it was observed that the same processing of the various types of Mg produced by different processes gave different shapes of particles and different distributions of particle size. Thus the rather symmetrical Permanente crystals gave approximate equiaxial granules while the New England Lime Co. muffs produced fibrous units. As a result the behavior of these particles in the screens did not really represent relative particle sizes or surface areas per unit of mass. Hence, a complete study of the effect of particle size on the yield was made using each type of Mg studied.

Also, different grinds were obtained at the various plants due to use of different cutting equipment. Some of these grinds were simulated by blending screened material. Other material was separated into fairly narrow limits by screening in order to study the effect of each size within as narrow limits as possible.

4.3.1 Specifications of Mg Used in Test.[24] In order that other variables be excluded all these lots were prepared from the same stock of New England Lime Co. muffs whose behavior had been found to be most consistent. Since the New England muffs could not be cut to simulate the shape of the dense Permanente, one lot of the latter was included. After cutting, screening and blending in an effort to obtain the above results, the final lots and blends were again analyzed for size distribution with the results shown in Table 5.

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TABLE 5

ACTUAL SCREEN ANALYSES OF PREPARED LOTS OF Mg

Designation	Per cent within Range Indicated					
	4-10	10-20	20-30	30-40	40-60	-60
a	1%	62%	22%	10%	4%	1%
b	1	44	23	18	12	4
c	1	55	26	13	5	0
d	2	75	13	9	1	0
e	85	15	1	1	0	0
f	1	67	24	6	1	1
g	0	1	20	38	34	8
h	0%	0%	0%	2%	43%	55%

Designation	Description of Prepared Lots.
a	Regular Grind of N.E.L. at Iowa State College
b	Blend to Simulate Electromet Grind of N.E.L.
c	Blend to Simulate Ames Grind of Permanente
d	Permanente Mg as Ground at Ames
e	+10 mesh, as screened, N.E.L.
f	10-20 mesh, as screened, N.E.L.
g	20-40 mesh, as screened, N.E.L.
h	40-60 mesh, as screened, N.E.L.

4.3.2 Results of Investigation.[25] The results of the test at a preheating temperature of 1200°F are summarized in detail in Table 6. The regular Ames grind, the simulated Electromet blend and the blend to simulate the size distribution of ground Permanente magnesium all gave comparable results with biscuit yields in the range of 95.5 per cent. Of the various narrowly sized fractions, best results were obtained with the 20-40 mesh fraction, which gave an average biscuit yield of 95.7 per cent. Magnesium from the Permanente Metals Corporation gave a biscuit yield of 92.4 per cent which was 3.3 per cent

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less than that obtained from New England Lime Company magnesium ground in the manner regularly employed at Iowa State College.

The performance of the Permanente magnesium in this series of tests was comparable with the performance of the Permanente material in the previous series of tests described under Section I. Permanente material was used in this program for control purposes in order to show whether operating conditions had changed during the period which had elapsed between the two test programs. Since comparable results were obtained on the Permanente material in both programs, it would appear that the conditions for both series of tests were essentially the same. It appears, therefore, that the New England Lime Company magnesium used in this test program, which gave biscuit yields in the range of 95-96 per cent, is inherently better than that from the same source used in the previous test program where yields in the range of 90-91 per cent were obtained.

The results of the runs at a preheating furnace temperature of 1250°F are also shown in Table 6. While biscuit yields are slightly lower (about 1 per cent) at the higher temperature, the relative performance of the various fractions of magnesium remained essentially unchanged.

4.3.3 Conclusions. It appears from the results shown in Table 6 that magnesium particle size within the limits of -10 to 40 mesh has no appreciable effect on biscuit yield. The differences in biscuit yield obtained from the various sized magnesium fractions are not sufficient to account for the relatively large differences in performance among the various types of magnesium tested in the program to evaluate the relative effectiveness of magnesium from different sources of supply covered in Section 4.2 of this report. It would appear, therefore, that the differences measured among the various types of magnesium in the previous test program were significant.

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TABLE 6

SUMMARY OF RESULTS AT
FURNACE TEMPERATURE OF 1200°F

Mg Type	Description	No Runs	Ave. Bisc. Yield	Ave. Cast Yield	Ave.* Over-all Yield	Ave. Firing Time Min.
a	Ames Reg. Grind, N.E.L.	15	95.7%	94.3%	90.2%	63
b	Electromet Blend, N.E.L.	15	95.3	93.5	89.2	55
c	Permanente Blend, N.E.L.	15	95.2	93.4	89.0	60
d	Permanente Grind, Perman.	15	92.4	91.3	84.3	75
e	4 - 10 N.E.L.	15	90.2	88.8	80.1	77
f	10 - 20 N.E.L.	15	94.7	93.3	88.3	65
g	20 - 40 N.E.L.	15	95.7	94.6	90.5	50
h	40 - 60 N.E.L.	7	93.9%	90.0%	84.5%	50

SUMMARY OF RESULTS AT
FURNACE TEMPERATURE OF 1250°F

a	Ames Reg. Grind, N.E.L.	12	95.0%	95.2%	90.5%	56
b	Electromet Blend, N.E.L.	12	93.8	93.9	88.2	53
c	Permanente Blend, N.E.L.	9	94.0	92.8	87.3	51
d	Permanente Grind, Perman.	12	92.2	93.8	86.5	71
e	4 - 10 N.E.L.	12	89.7	90.2	80.8	69
f	10 - 20 N.E.L.	12	94.6	94.2	89.1	55
g	20 - 40 N.E.L.	12	94.8	94.8%	89.8%	47
h	40 - 60 N.E.L.	1	89.1%	----	----	40

*Product of Biscuit and Casting Yields

LIME LINER

Bottom, 6" from bottom - 3% Mg in Ste. Genevieve Lime

Side , 3" from top - 1% Mg in Ste. Genevieve Lime

Top , Kelly Island Dolomite, No Mg.

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5. Processing and Specifications of Liner Refractories

5.1 Purpose of Liner. The steel bomb or reaction chamber was lined with an inert material (1) to protect the metal from contamination by the iron of the bomb and (2) to protect the bomb from attack by magnesium and uranium at the temperatures produced by the reaction.[23] Hence, it was necessary that the liner material have the following characteristics: (1) refractory, stable at temperatures up to 1800°C in some cases, (2) chemically inert, non-reactive with either reactants or products, (3) pure, at least with respect to reactive substances or forbidden elements as boron or cadmium.

5.2 Possible Refractories. The first requirement, stability and infusibility at the maximum temperatures, eliminated most halides and oxy-salts and suggested particularly certain metallic oxides, carbides, and silicates. The second requirement, chemical inertness, eliminated the silicates which are vigorously reactive with Mg and the carbides, also reactive with other metals. This left only the refractory metallic oxides for consideration, particularly CaO, MgO, Al_2O_3, BeO, ZrO_2, ThO_2 and a few others. Al_2O_3 and ZrO_2 were found to be reactive with the products and BeO and ThO_2 were too limited in availability to consider; hence the field was narrowed down to CaO and MgO or to mixtures of the two such as dolomitic lime. The product chosen must be available in quantity and of the necessary purity. Commercial lime of adequate purity was found and was adopted for production by both the Ca and Mg processes.

5.3 Effect of Water in Liner Refractory on Yield of U. From the beginning of operations with Ca and continuing into production with Mg[26] wide fluctuations in the shape and size of the metallic ingot, its freedom from slag incrustations and inclusions and in the yield occurred with the use of different shipments of liner refractory, presumed to be the same product. The evolution of hydrogen gas shown by hydrogen flames at the cover of the bomb before and during reaction suggested the presence of water in the high-calcium lime originally used. Analyses showed as much as 2.5 per cent ignition loss, later shown to be largely water. Discussions with the manufacturers of the lime (Ste. Genevieve Lime Co., St. Louis, Mo.) resulted in a prolonged burn in the vertical kilns,

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followed by hand picking and coring which produced a more consistent product. However, even high-burned lime has considerable tendency to take on water and the difficulties were not removed on the above treatment.

The production of brown oxide on the surface of the ingot and slag when hydrogen flames indicated water in the lime suggested that the heating of the tetrafluoride in the presence of water resulted in hydrolysis of the fluoride to the brown oxide which is not reducible in the bomb.(27) If so, the hydrogen fluoride produced would diffuse through the charge to the lime liner, react with CaO to form water which in turn would hydrolyze more UF_4.

$$2\ H_2O + UF_4 \text{ ---------- } UO_2 + 4\ HF$$
$$4\ HF + 2\ CaO \text{ ---------- } 2\ CaF_2 + 2\ H_2O$$

Only by this cyclic mechanism could the small amount of water present (never more than 0.34 lbs., 2 per cent of the weight of the lime in the liner) convert the entire charge of 56 lbs. of UF_4 to UO_2, which would require 6.4 lbs. of water.

The occurrence of this cycle of reactions was demonstrated by heating a series of charges of UF_4 in small bombs with lime liners but without Mg mixed with the UF_4.(28) Conversion to brown oxide (UO_2) started at the lime-fluoride interface and progressed inward with a very sharp "front" finally going to completion if heated long enough. Analysis of the liner revealed the presence of fluoride in the lime, showing that the second reaction had occurred, regenerating water.

5.3.1 Use of Mg in Liner to overcome Effect of Water.(28) Assuming this cycle of reactions, Mr. David Peterson mixed some finely ground magnesium in the lime to convert the water to hydrogen and thus stop the cyclic reaction. One per cent by weight of Mg in the lining material produced a yield of 91.9 per cent and 6 per cent of Mg in the liner produced a yield of 94.7 per cent under conditions and with products whose average yield without Mg in the liner was only 84.6 per cent The time of preheating before ignition decreased from an average of 114 minutes to about 60 min. A series of experimental runs were made with

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magnesium contents of 0, 3 and 5 per cent Mg in the liner to determine the optimum content. Results are shown in Table 7.

TABLE 7

EFFECT OF Mg (50-100 MESH) IN CaO BOMB LINERS

Run Numbers	No. of Shots	% Mg in Liner	Firing Time	% Yield
6098	1	1%	--	91.9%
6193	1	6	--	94.7
6092-6137	44	0	114 min.	84.6
6215-6256	42	5	55	90.8
6257-6289	33	3	57	90.0
6290-6345	56	0*	78	85.3
6346-6357	12	3	58	92.9
6358-6363	6	2	63	92.9
6372-6404	33	1	80	90.2
6405-6436	32	0	74	88.8
6437-6443	7	3	66	94.3
6447-6493	45	0%	75 min.	87.6%

*Bracketed groups are comparable in all regards except Mg content in wall. Liners containing 0% Mg were used for comparison.

It will be observed that 3 to 5 per cent Mg increased the yield by as much as 5 per cent and decreased the firing time by 10 to 30 minutes. The use of Mg in the liner was then tried out in production over a trial period of several weeks. The following table of weekly averages of production yield demonstrates the effectiveness of the procedure.

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TABLE 8

Period	Average Yield	Lining
May 6 - May 12, 1943	85.8%	No Mg in Lining
May 13 - May 19	81.6	" " " "
May 20 - May 26	85.1	" " " "
May 27 - June 2	85.7	" " " "
June 3 - June 9	----	Transition, Testing period
June 10 - June 16	88.3	3% Mg in Lining
June 17 - June 23	88.8	3 " " "
June 24 - June 30	89.2	4 " " "
July 1 - July 3	89.7	4% " " "
July 9 - July 15	86.5%	No Mg in Lining

It will be noticed that prior to the use of Mg the yields were 85.0 to 85.8 per cent, 85.7 per cent the week before adoption. After a week of testing and comparison, the use was adopted for regular production, with an increase of 2.4 per cent the first week to 3.1 per cent the next week. The rise continued to 89.7 per cent when the use of Mg was discontinued as a check. On discontinuing the use of the Mg the yield dropped to 86 per cent, a drop of 3.2 per cent. Over this entire period the use of Mg in the lining was accompanied by a general increase of 3 per cent in yield and by the production of cleaner biscuits. Several subsequent studies of this effect verified these findings, establishing 3 per cent Mg as the quantity needed with most lime, with an average increase in metal yield of 3 per cent using standard products. The preheating period or firing time was found to be much more consistent when Mg was used, varying from 55 to 180 minutes without Mg in the liner, but varying only from 55 to 65 minutes with Mg.(30)

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5.4 Investigation of Various Refractories as Liner Material. Although the addition of Mg to the liner improved the yield and the behavior of the reduction reaction greatly, occasional deviations still occurred. Further analytical studies revealed that the CO_2 content of the lime was also extremely variable being a function of the lump size and geological nature of the limestone as well as of the burning procedure.

In the effort to avoid the ill results occurring from both water and carbon dioxide in high-calcium lime a number of other refractories were tried. On the assumption that high-burned dolomitic lime was more "dead-burned" with less tendency to pick up water than high-calcium lime, its use was investigated. Fused lime should have been free of CO_2 and H_2O, but was not commercially available. The Electro Metallurgical Company fused some dolomitic lime in the electric arc furnace[31] and some of this product was supplied to Iowa State College. At the request of the writers Electro Met later fused some high-calcium lime. Fused magnesia[32] has no tendency to hydrate, hence should eliminate the water problem, at least, provided it should prove otherwise usable. At various times these different refractories had been tested as bomb liners, but finally a very comprehensive program was conducted in February 1944.[33]

5.4.1 Refractories Investigated; Particle Size, Packing Density and Purity. The following materials were used in this investigation:

(1) Ste. G.; High-calcium lime, Ste. Genevieve Lime Co.

(2) K.I.D.; Dolomitic lime, Kelley Island Lime & Transport Co.

(3) E.F.D.; Electrically fused dolomitic lime, Electro Metallurgical Co.

(4) MgO ; Electrically fused magnesium oxide, General Electric Co.

These products were reduced in various ways to the size distribution shown in Table 9.[34]

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TABLE 9

PARTICLE SIZE OF LINER REFRACTORIES AS USED

	Percent passed by Sieve No.				
Refractory	60	80	100	200	325
MgO	99%	98%	94%	63%	27%
EFD	100	99	99	50-60	10-20
K.I.D.	75-97	15-25	9-15	1-3	0-1
Ste. G.	99%	96-97%	80-90%	70-80%	35-50%

Since the heat conductivity and therefore the insulating properties of these refractories vary with their packing densities, the latter were determined by packing equal volumes of each refractory in a small bomb on the jolting table. A steel piston weighing 1 lb., 2 oz. was placed on top of the charge during packing. Each charge received 500 blows of the packer.

TABLE 10

PACKING DENSITIES OF LINER REFRACTORIES

	Method of Preparation		
Refractory	Com'l Burn	Sintered (1700°C)	Fused
MgO			2.26 (G.E.)
Dolomitic oxide	1.33		2.00 (E.F.D.)
CaO (lime)	1.43	1.75	1.88 (E.F.L.)

The significant impurities present in the various types of refractories were determined and found to be as follows:

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TABLE 11

IMPURITIES IN VARIOUS LINER REFRACTORIES[34]

Refractory	CO_2	H_2O	B	Cd	Fe	Mn	Si
MgO	.09%	0.01%	3-4 ppm	<5 ppm	235 ppm	<10 ppm	2%
E.F.D.	.06-0.10	0.14	3-7	<5	400-700	60-100	
K.I.	0.03-0.25	0.35-0.39	4-15	<5	65-500	70-90	
Ste. G.	0.05-0.30%	0.13-0.60%	1-14 ppm	<2 ppm	100-600 ppm	30-60ppm	%

5.4.2 Procedure Used in Investigation.[35] The liner refractories were first tested in a series of runs (Series I) in which the entire liner was made of the same refractory. This series revealed the mechanical and technical advantages and difficulties encountered in handling each product. A second series consisted of combinations of the various refractories used in different portions of the bomb. Since it had been observed that various refractories behaved differently in a given section of the liner, the liner was divided into sections as shown in Figure 1 designated in the figure and text as follows:

B. "Bottom," including bottom layer and lower 8" of side wall, in which section biscuit and slag collected. This section was subjected to prolonged heating after reaction occurred.

S. "Side wall", including wall from 8" above bottom to 10" below top, extending about 18" in height.

TS. "Top, side", including upper 10" of side wall.

Tc. "Top, center", including refractory packed on top of charge

Ts and Tc are simply designated as "Top", if no difference is made.

It had also been observed that varying percentages of magnesium fines were advantageous in different positions in the bomb. Thus 3 per cent of magnesium fines usually gave optimum results in the bottom of the bomb, while only 1 per cent was needed in the side wall. Hence, the quantity of magnesium fines was also varied from 0 to 3 per cent in

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various portions of the liners and in the different refractories in the composite liners.

From each series the best liner components were selected and regrouped into new combinations until all promising combinations of refractories and of magnesium content had been tried out.

The liners of a given series were alternated in the loading and firing operations in order to eliminate the human and plant variables. One or more types of the preceding series were run in each new series as a check on the constancy of other factors. Standard UF_4 and Mg were used and other factors were kept constant. The furnace temperature was 1200°F.

5.4.3 Results.[36] The complete results of all the liner combinations investigated in this study are reported fully elsewhere.[37] Only those of significant interest, either in yield or cost, will be included here, summarized in Table 12. In Series I (Table 12) are the yields of uranium and cost of liner per pound of metal using liners of the same material throughout. In Series V, VI and VII various combination liners were used.

Over-all yield reveal the fact that electrically fused dolomitic lime with 3 per cent Mg produced the highest yield in the first series of runs although in subsequent series in the program high-calcium lime produced equally well. The MgO without Mg fines produced well, but due to its lack of cohesion even on long packing it offered such difficulty that its use in production was not practical. Its extremely high relative price precluded its use in any case unless it should have been found to have advantages over the other types, which it did not have.

The kiln-burned dolomitic lime (K.I.D.) gave poorest results (83.3% over-all as compared with 87 to 91% by the other products) although slightly improved by the use of 3% Mg fines (83.3 to 85.6%). A number of efforts to use kiln-burned dolomitic lime at Iowa State College and elsewhere consistently gave the same results -- slag encrusted ingots of metal, enlarged beyond the original diameter of the reaction space in the packed liner and with protruding fins sometimes reaching to the bomb wall. This indicated considerable shrinkage or perhaps melting of the dolomitic oxide at the temperature of the metal, the wetting of the metal and the

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TABLE 12

COMPARISON OF YIELDS OF U AND COST OF LINER USING VARIOUS REFRACTORIES

Series	Type	Liner Sections			Biscuit Yield	Cast. Yield	Over-all Yield	Cost Liner Cents	Cost Liner /lb. metal cts.
		Bottom	Side	Top					
I	1	MgO, 0%	Overall		94.6%	94.9%	89.7%	1487 cts.	39.8 cts.
	2	MgO, 3	"		93.0	94.3	87.7	1433	39.2
	3	E.F.D. 0	"		88.4	95.2	84.1	348	9.94
	4	E.F.D. 3	"		95.3	95.8	91.3	329	8.65
	5	Ste.G. 0	"		93.1	93.9	87.3	63	1.73
	6	Ste.G. 3	"		92.6	94.2	87.2	61	1.68
	7	K.I.D. 0	"		89.1	93.5	83.3	31	.89
	8	K.I.D. 3	"		90.7	94.4	85.6	30	.84
V	1	E.F.D. 3	E.F.D.3%	E.F.D.3%	95.8	95.3	91.3	366	9.63
	2	Ste.G. 3	"	"	96.7	96.4	93.2	281	7.24
	3	"	"	" 0	96.4	96.0	92.5	288	7.47
	4,5	"	" 0%	E.F.D.0	98.2	96.9	95.2	296	7.47
	6	"	Ste.G.0%	E.F.D.0	97.9	96.6	94.5	174	4.42
	7	"	E.F.D.0%	E.F.D.0	97.7	96.7	94.5	296	7.52
	8	"	Ste.G.0%	Ste.G.0	97.3	96.2	93.6	66	1.69
	9	"	Ste.G.1%	"	96.5	96.1	92.7	66	1.71
	10	"	"	K.I.D.0	97.1	97.3	94.6	54	1.37
	11	E.F.D. 3	"	"	96.8	97.0	93.9	140	3.58
	12	"	"	Ste.G.0	96.5	97.1	93.7	152	3.89
VI	1	Ste.G. 3	Ste.G.1%	K.I.D.0	96.4	96.1	92.6	50	1.30
	2	"	E.F.D.1%	"	94.5	97.1	91.6	173	4.53
	3	"	"	"	96.8	96.6	93.5	173	4.45
	4	E.F.D. 3	Ste.G.1%	"	96.8	95.9	92.6	136	3.53
	5	"	E.F.D.1%	"	95.0	96.4	91.6	259	6.79
	6	" %	"	" %	96.8%	96.7%	93.6%	259 cts.	6.65 cts.

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Table 12 (continued)

Series	Type	Liner Sections Bottom	Side	Top	Biscuit Yield	Cast. Yield	Over-all Yield	Cost Liner Cents	Cost Liner /lb. Metal Cts.
VII	1	Ste.G. 3%	Ste.G.1%	Ste.G.0%	96.9	96.0	93.0	59 cts.	1.63 cts.
	2	"	"	E.F.D.0	97.8	96.3	94.2	131	3.34
	3	"	"	KID(St.L)	95.3	97.0	92.4	51	1.33
	4	"	"	"(sacks)	95.1	96.6	91.9	51	1.33
	5	"	"	"3% "	95.0	96.7	91.0	51 cts.	1.33 cts.

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cracking radially of the contracting liner. The contraction resulted from the greater density of the more highly sintered wall, which left a larger cavity at the bottom of the bomb and which cracked in circumference on shrinking. Iron contamination increased and low yields were obtained in both reduction and casting stages. Pitting of the bombs and "burn-outs" were much more frequent.

The electrically fused dolomitic oxide showed least reaction with the product producing very smooth-surfaced, clean ingots of metal with little adhering slag which resulted in high casting yields. Since volume changes had already occurred in the fusion, fused refractories including MgO and CaO showed least volume change and adhesion to metal.

Properly burned high-calcium lime such as Ste. Genevieve, showed some shrinkage as compared with E.F.D. but very little as compared with dolomitic lime. Biscuits were clean and free of fins.

5.4.4 Conclusions.[38] The yields obtained with the various types of liners are so nearly the same that on a basis of cost of liner per pound of metal produced the costs are practically proportional to the costs of the refractories used.

Refractory	Series	Type	Cost of Liner Per Lb of Metal	Cost Refractory Cts/Lb
MgO	I	1	39.8 cts.	52.0 cts.
E.F.D.	I	4	8.65	13.5
Ste. G.	V	8,9	1.71	3.3
Ste. G., K.I.D. top	V	10	1.37	—
K.I.D.	I	8	.89 cts.	1.65 cts.

On this basis alone dolomitic lime throughout would appear to form the most economical liner.

However, the cost of the bomb liner is one of the smallest costs involved in the various stages of processing of the uranium from ore to metal. The production of low yields and the contamination of much of

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the metal by iron due to pitting of the bombs causes the small saving in cost per pound of metal to be much more than offset by the cost of recycling unrecovered element and by the loss of useful metal by contamination.

The next cheapest liner, Ste. G. bottom and side and K.I.D. top, (Series V Type 10) had produced excellent results at Iowa State College for some time in regular production both with respect to over-all yield and purity. Hence if it could be consistently obtained, this liner was the most economical producer of uranium of highest quality.

However, the experience at Ames had demonstrated that commercial lime producers were not in position to supply a consistently burned product over a period of time. A comparison of weekly averages over a period of time during which all other products and conditions were constant and the same brand of high-calcium lime was used as liner, but different shipments of lime were used corresponding approximately with the weekly periods demonstrated this variation.

	Biscuit Yield	Casting Yield	Over-all Yield
Feb. 17-Feb. 24, 1944	96.3%	95.1%	91.6%
Feb. 24-Mar. 2, 1944	95.9	95.9	92.0
Mar. 2-Mar. 9, 1944	93.6	94.2	88.2
Mar. 9-Mar. 16, 1944	91.3	94.6	86.4
Mar. 16-Mar. 23, 1944	93.8%	94.4%	86.6%

It will be noted that the above decrease in yield came with the advent of increased humidity in the spring. This stressed not only the fluctuation in the water content of the purchased product, but the very great tendency of burned lime to absorb atmospheric moisture. Even the utmost precautions in packing and handling were not sufficient to protect the lime during the humid months of spring and summer as long as grinding, mixing and packing had to be done in unconditioned air.

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Therefore, in spite of the lower cost of the high calcium lime and its equal performance when correctly burned and handled, it was decided to adopt electrically fused dolomite as the refractory bomb linings in regular production. A general increase in weekly yields and decrease in boron and iron contamination followed this change due to greater stability of the liner and less contamination by the impurities of the liner and by the iron of the bomb.

5.5 Specifications. The final specifications of the liner refractory for use at Ames were: electrically fused dolomite, ground to pass 50 per cent or more through 200 mesh screen and not more than 20 per cent through 325 mesh screen; not to contain more than 15 ppm of B, 5 ppm of Cd, 1000 ppm of Fe, 100 ppm of Mn, 0.1% CO_2 or 0.30% H_2O. Most of the E.F.D. supplied came well within these specifications.

6. Conditions of Operation

The establishment of optimum operating conditions occurred gradually with the acquisition of equipment and materials. In fact such conditions as preheating temperatures and excess of magnesium varied so greatly with raw materials that operating conditions could be fixed only in terms of specific materials. However, many conditions ultimately were fixed and those conditions and their experimental verification will now be described.

6.1 Mixing of Charge. From the early mixing of charges of a few hundred grams of reactants with a spatula to the mechanical mixing of charges of several hundred pounds it was observed that thorough mixing of the charge was essential to complete reaction and separation of products. The MacLellan type of batch mixer was found to be well suited to these materials and a motor-driven one-cubic-foot capacity mixer was installed. It was established that a least four minutes of mixing at 6 turns per minute in this mixer was necessary. An incomplete mixture resulted in low yield and slag-encrusted biscuits.

6.2 Thickness of Liner. The thickness of the liner determined (1) the rate of heat input, (2) the rate of heat loss on cooling, (3) ignition time, and (4) total heat input on preheating. As a result of control of total heat input and of rate of cooling too thin a liner

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could cause inadequate heating and too rapid cooling both resulting in incomplete reduction and separation of metal and low yields. Also too thin a liner would not offer the protection to the bomb for which the liner was used. Since some washing away and penetration of the liner by slag occurred safety dictated a minimum thickness of 3/8" in the 6" bomb and about 1/2" in larger sizes. In smaller bombs 1/4" liners have been used.

On the other hand too thick a liner resulted in too slow heating and the occurrence of side reactions during the prolonged heating period. Also too thick a liner had a tendency not to pack as well and to crack or wash away. For these reasons liner thicknesses between 3/8" and 1" were investigated.(34) A tapering mandrel was built which produced a wall 3/8" at the top and 1/2" at the bottom. Another mandrel produced a wall 5/8" thick at the top, 3/4" thick at the bottom. The thicker wall increased firing time so greatly that it was necessary to raise the temperature of the furnace to 1300°F to produce reaction in reasonable time. Results of the two walls at 1300°F are tabulated below.

Wall Thickness (Near Bottom of Bomb)	Firing Time	Yield
1/2"	75 min.	82.5%*
3/4"	90 min.	77.4%

*These values were obtained in early production when yields were low. Subsequent trials established a 7/16" to 1/2" wall as standard.

6.3 Excess of Magnesium. In the first experimental reductions of UF_4 by Ca 50 to 100 per cent excess of Ca was used. As purer, less oxidized Ca and purer tetrafluoride became available and more knowledge of proper particle size was gained, it became possible to decrease this excess. Since the excess represented increased cost of production and since the residue in the crude metal offered considerable interference and danger in casting, it was very desirable to decrease the excess of reducing metal as much as possible.

To determine exactly the optimum excess in the 6" bomb a series of

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reductions were made varying the excess from 0 to 15 per cent.(40) Since the use of over 15 per cent of magnesium was very bothersome and even dangerous in the casting process due to the ignition on exposure to air of the finely divided distilled magnesium condensed on the head of the vacuum system, excesses over that amount were not considered further.

Results are tabulated on Table 13 and shown graphically in Figures 5 and 6.

TABLE 13

EFFECT OF EXCESS OF Mg ON YIELD OF U

Per cent Excess Mg	Ave. Biscuit Yield	Ave. Casting Yield	Ave. Over-all Yield	Ave. Firing Time
0%	85.1%	76.6%	65.2%	57.3 min.
2½	92.7	90.2	83.6	52.3
5	96.2	94.9	91.3	51.4
7½	96.8	95.7	92.6	49.9
10	96.8	95.2	92.2	49.7
15%	96.3%	96.5%	92.9%	49.6 min.

6.3.1 Results. It will be observed from Table 13 and Figure 5 that in the reduction stage the optimum yields were obtained with excesses of 7.5 per cent and 10 per cent magnesium or with a maximum of 8.75 per cent excess magnesium. From Table 13 and Figure 6 it is apparent that in over-all yield a plateau was reached at 7½ per cent excess of magnesium. The 15 per cent excess of magnesium gave a very slight increase in the over-all yield. From Figure 7 it is also apparent that in the reduction reaction there was a relationship between the excess of magnesium and the firing time or preheating time. As the excess of magnesium was increased the firing time was decreased. There was very little change in the firing time after an excess of 7½ per cent was reached.

6.3.2 Conclusions. From the curve shown in Figure 5 it appears that the maximum yield was obtained in the reduction stage under the operating conditions described at about 8½ per cent magnesium. However, from the over-all yields (Figure 6) it appears that very little difference

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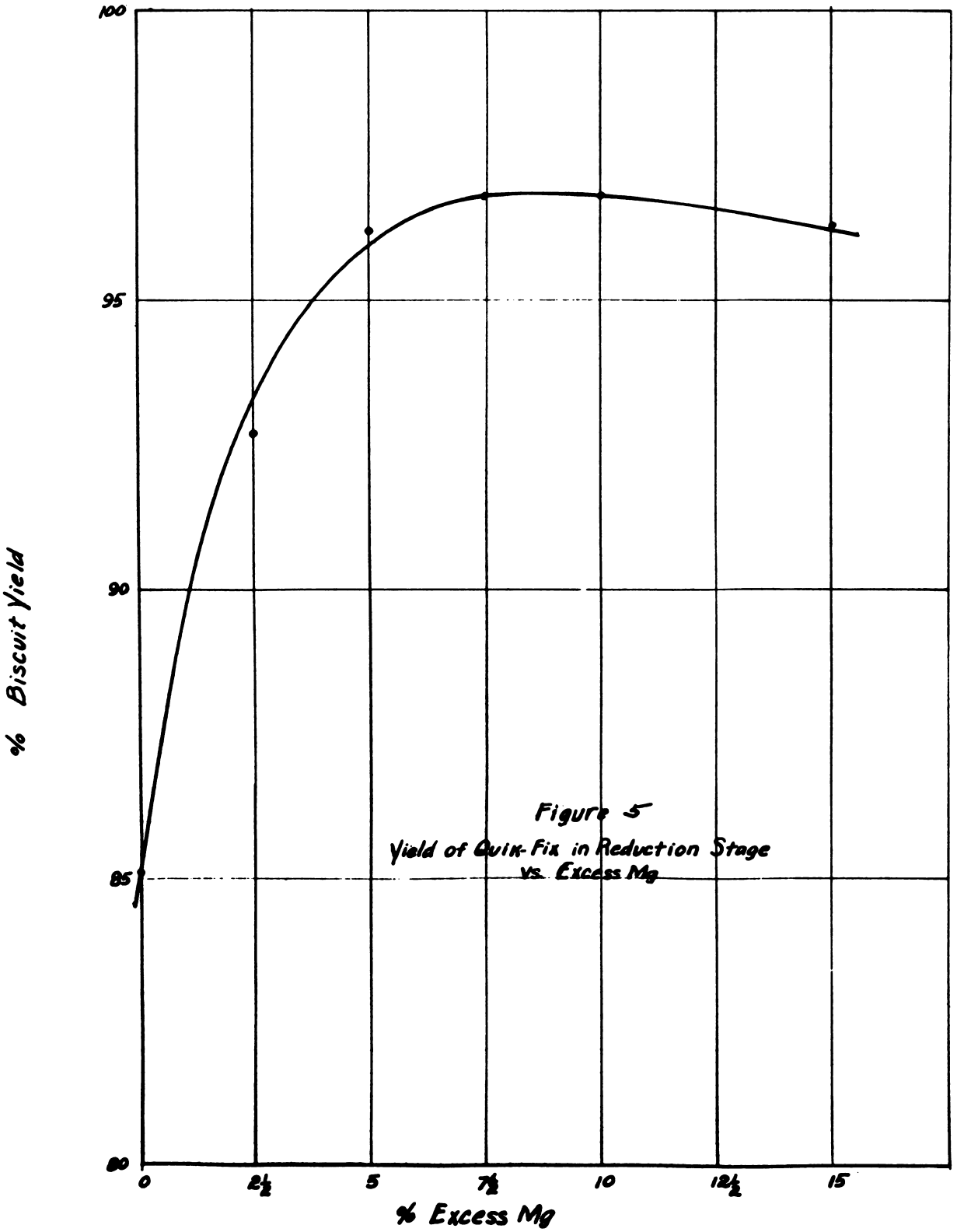

Figure 5
Yield of Quik-Fix in Reduction Stage
vs. Excess Mg

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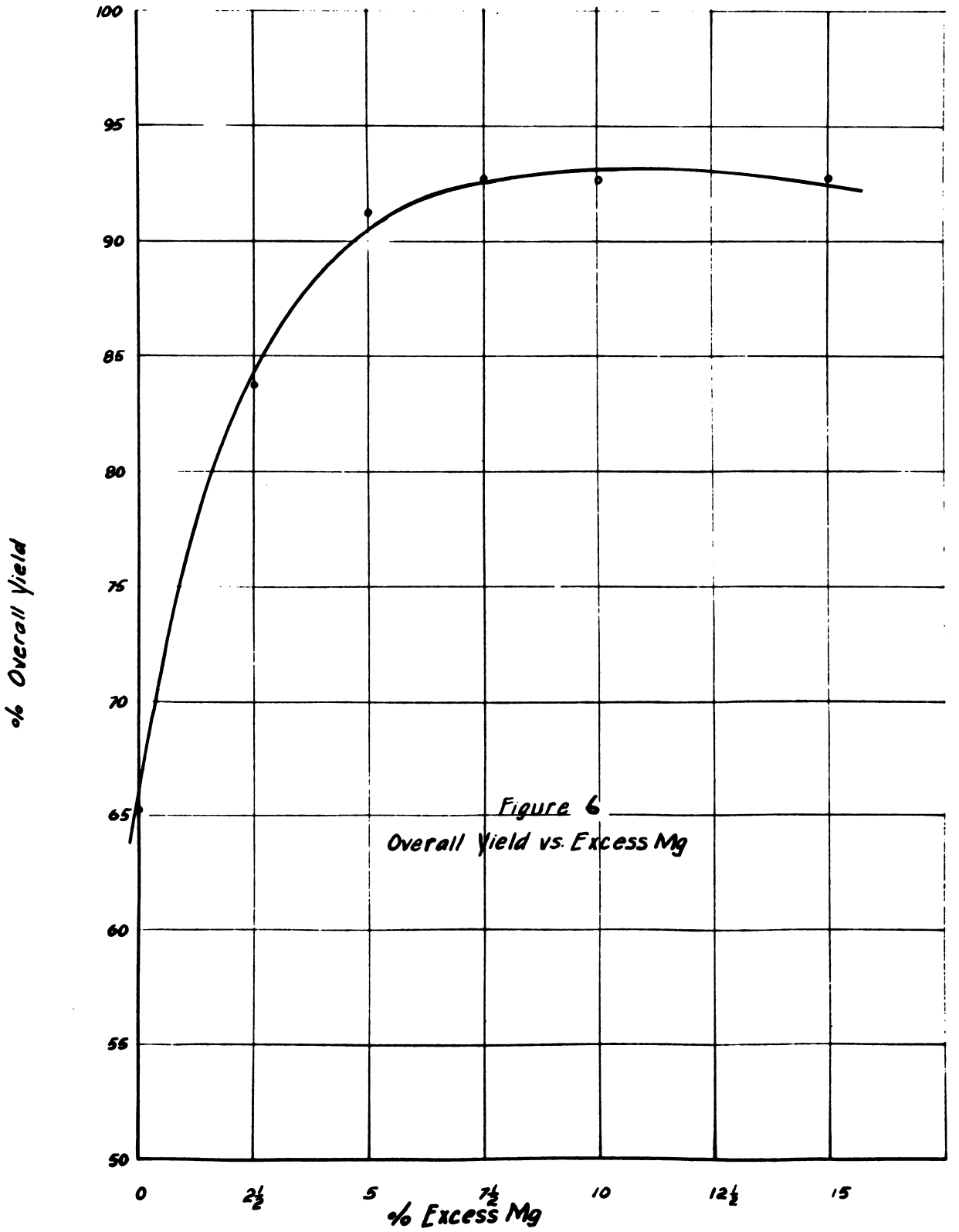

Figure 6
Overall Yield vs. Excess Mg

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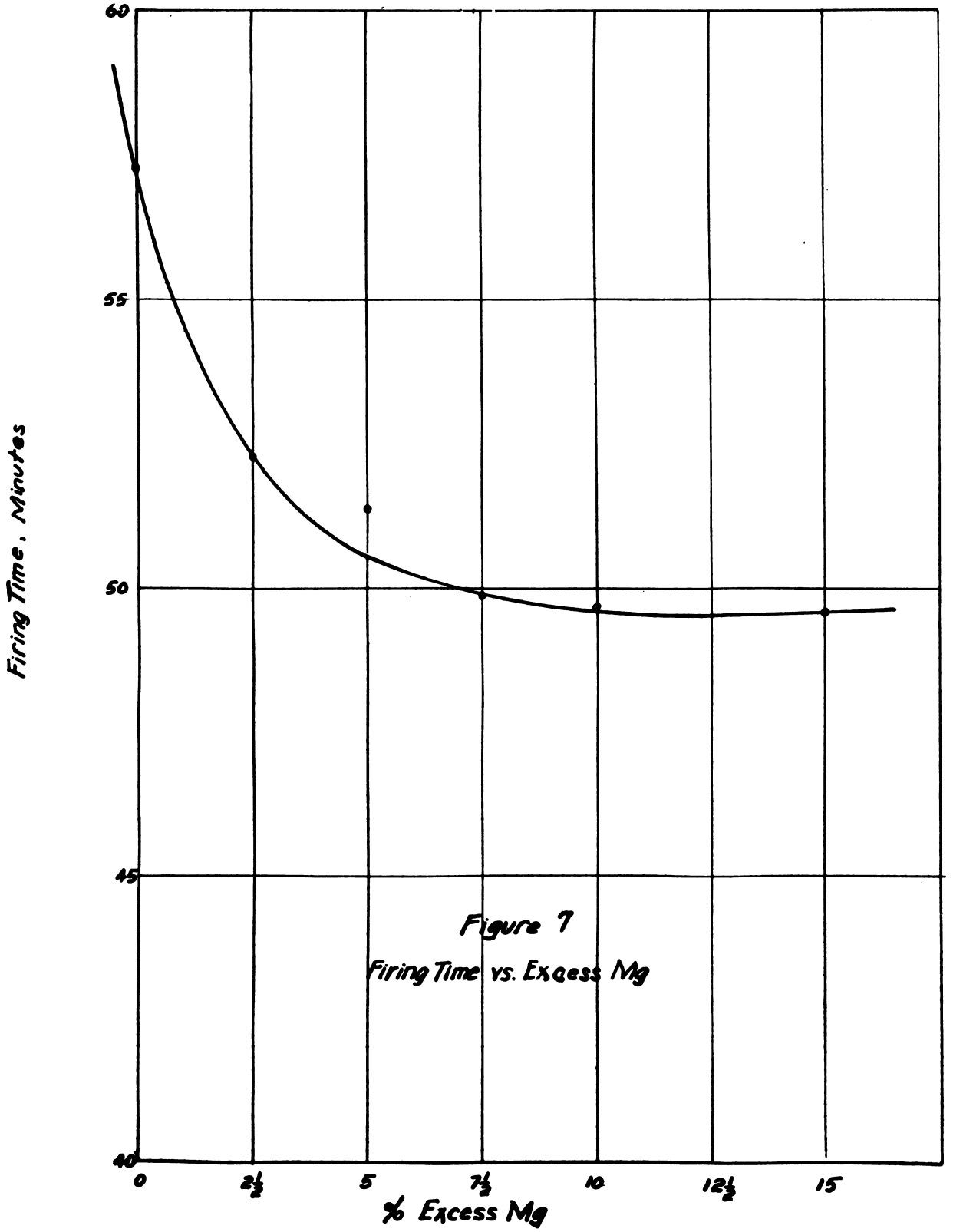

Figure 7

Firing Time vs. Excess Mg

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occurred from 7½ to 15 per cent deviations in both biscuit and casting yields being sufficiently large to indicate that the average over-all differences from 7½ to 15 per cent were not real. Since unnecessary excess caused trouble in casting and represented additional cost, 7½ per cent excess, the minimum excess producing yield, was adopted as standard for the 55 lb. charge of UF_4 used in the 6" bomb. It must be borne in mind that the excess varies with the scale of operation, being related to the heat input and heat loss. Thus, with the 133 lb. charge used at Mallinckrodt Chemical Works only 5 per cent excess magnesium is necessary while on a scale of a few pounds from 20 to 30 per cent excess of magnesium has been found necessary for maximum yield. The 7½ per cent excess was adopted as standard procedure for the 6" bomb at Iowa State College.

6.4 Effect of Preheating Furnace Temperatures. In the early production period it was observed that different furnace temperatures were required to achieve maximum yields with various lots of a given raw material such as magnesium. Consequently when the performance of the various types of magnesium was studied the effect of furnace temperature was investigated by making a series of reductions at intervals of 50 degrees from 1050°F to 1300°F. (See section 4.2.2).

The results of this study are presented in Tables 14 and 15 and Figures 8 and 9.

It will be observed (Table 14) that with one exception the optimum furnace temperature was found to be approximately 1150°F. At this temperature, however, the firing time of one type of Mg (Permanente) was about 60 minutes while that of the other types was about 50 minutes. The Permanente Mg always exhibited this slower rate of ignition. The optimum temperature for the Permanente was found at other times to be as high as 1300°F.

The relation of yield to firing time is shown graphically in Figures 8 and 9. Figure 8 presents the average firing times of each type of Mg at the designated furnace temperature. Since such irrelevant factors as accidental variations of wall thickness, dryness of the liner, etc., might cause abnormal deviations from the average firing time, it was decided to plot only those cases showing deviation within specified limits on the assumption that they represented the true value for the Mg in

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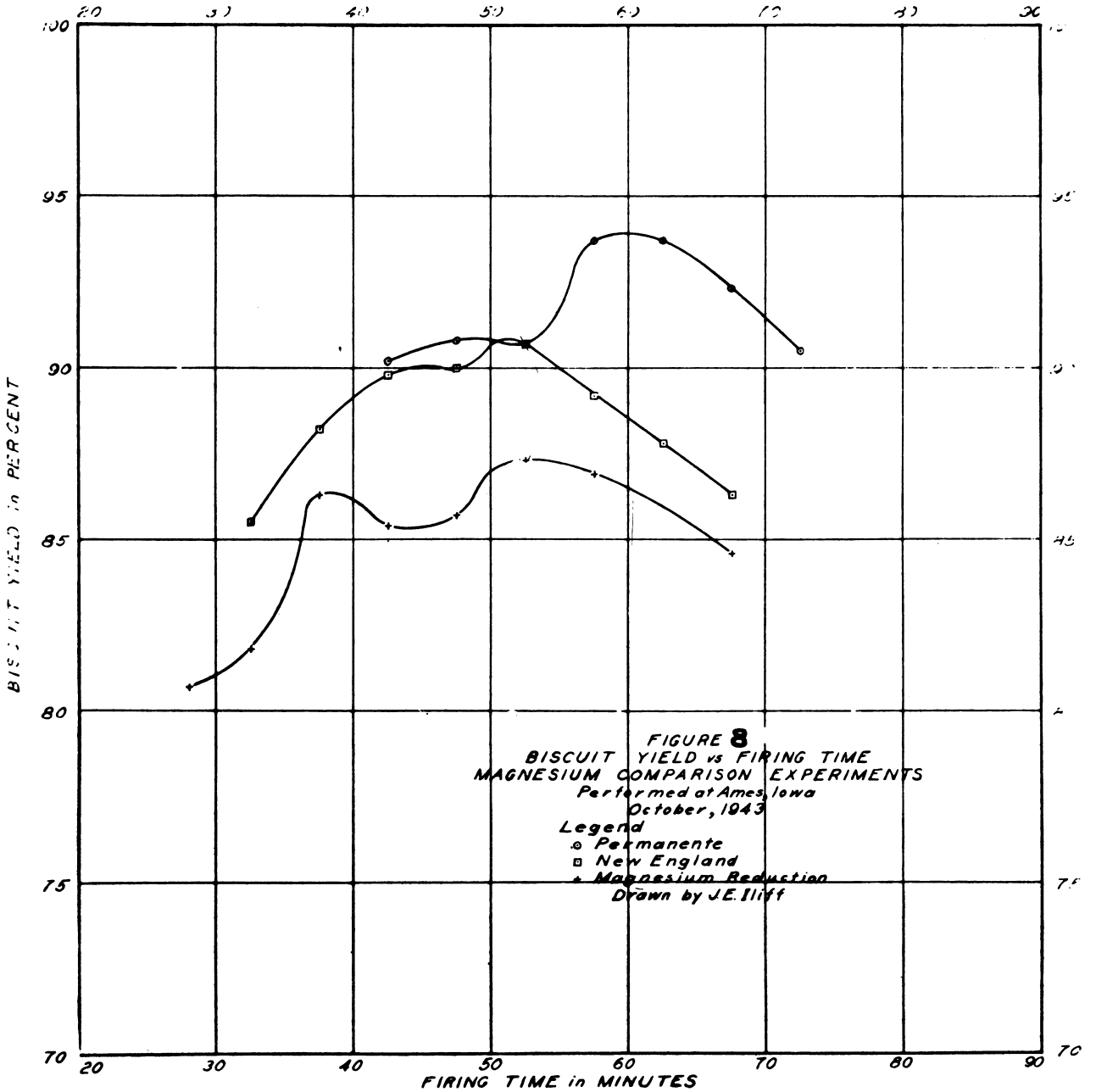

FIGURE 8
BISCUIT YIELD vs FIRING TIME
MAGNESIUM COMPARISON EXPERIMENTS
Performed at Ames, Iowa
October, 1943
Legend
⊙ Permanente
□ New England
+ Magnesium Reduction
Drawn by J.E. Iliff

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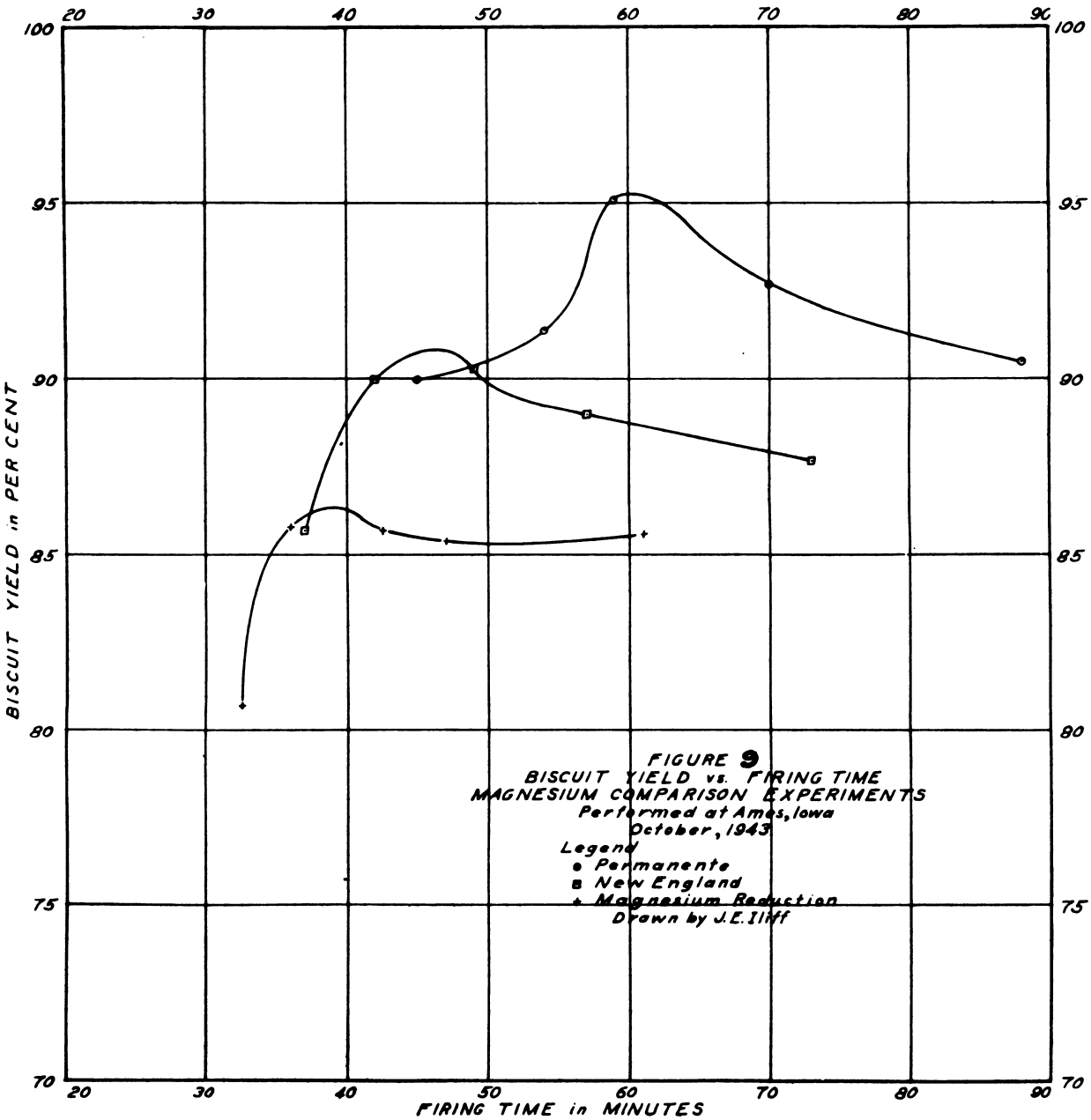

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TABLE 14

OVER-ALL YIELDS OF U PRODUCED BY VARIOUS TYPES OF Mg AT GIVEN FURNACE TEMPERATURES

	Temperature of Preheating Furnace					
Type Mg*	1050°F	1100°F	1150°F	1200°F	1250°F	1300°F
I	86.9%	88.9%	89.9%	84.4%	86.3%	86.9%
II	83.8	90.3	92.0	85.8	83.4	83.7
VII	----	----	----	87.4	----	----
III	81.5	85.0	86.0	84.2	84.2	82.1
IV	84.7	85.6	86.8	85.8	85.8	82.7
VI	84.7	84.0	83.8	84.7	----	79.1
V	81.0%	81.3%	78.3	76.9%	75.0%	75.6
VIII	----	----	81.2%	----	----	74.5%

TABLE 15

PREHEATING TIME (FIRING TIME) AT GIVEN FURNACE TEMPERATURES

Type Mg*	1050°F	1100°F	1150°F	1200°F	1250°F	1300°F
I	90 min.	70 min.	58 min.	53 min.	—	44 min.
II	88	69	59	54	—	47
VII	—	—	—	56	—	—
III	75	59	53	43	—	38
IV	68	56	47	42	—	35
VI	76	56	47	41	—	38
V	61	47	42	36	—	31
VIII	— min.	-- min.	42 min.	— min.	—	34 min.

* See Page for key to types.

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question. Hence, only those values falling within a 5 minute range including the greatest number of cases were averaged and plotted in Figure 9. The greater validity of this treatment is shown by the disappearance of the double maxima in some of the curves. The results obtained indicate optimum time for the Magnesium Reduction Co. Mg of 40 minutes as against 50 minutes by the first set of averages.

Having established the existence of an optimum furnace temperature, or rather perhaps an optimum preheating time or preheating rate, it was observed that control of preheating time could very effectively be used as a means of controlling production yield, provided that it was kept in mind that preheating or firing time varied with the different materials such as the types of magnesium in use and particularly with liner materials. For any change of raw materials therefore it was necessary to establish experimentally the optimum furnace temperature and preheating time (Figure 10). When this had been done any deviation of more than five minutes from the average heating time indicated that some raw material was defective, that standard operational procedures were being deviated from, or that the furnace was not operating properly due to defective burners, air-gas mixture or other difficulties.

The factor most frequently requiring a variation of the firing time was the condition of the liner material, particularly with respect to water content. The firing time actually used in any case was a compromise between a sufficiently long time for adding the necessary heat and the least possible time during which detrimental side reactions, such as $H_2O + UF_4$, might occur. If none of the latter reactions had occurred, i.e., if all raw materials had been perfectly pure and dry, a longer time than the minimum presumably would have been harmless. Since this condition was not achieved the preheating time could not be extended indefinitely without damage. As better liner material became available however the permissible limits became less critical and the time became more constant at a given temperature.

In spite of the many variables involved it was possible to adopt a furnace temperature of $1200^{\circ}F \pm 25^{\circ}$ as standard for production using New England Lime Co. Mg, UF_4 and electrically fused dolomite liners

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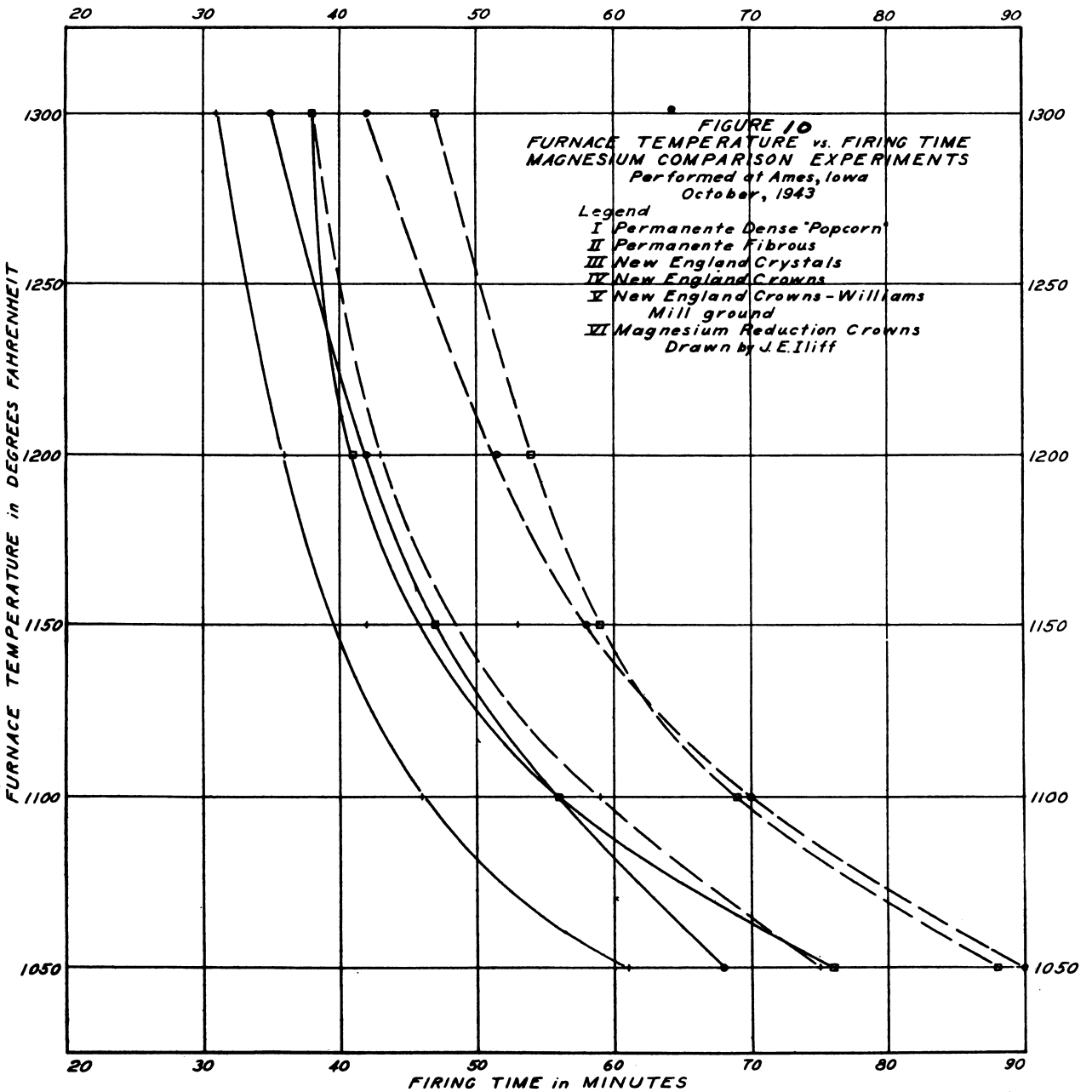

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meeting the specifications established in previous sections of this report.

6.6 Methods of Preheating. Various methods of preheating were used at different plants including electrical resistance furnaces, low-frequency induction furnaces, gas-heated furnaces for individual bombs and gas-heated multiple furnaces. Space does not permit here of a full comparison of these means of heating. General results are apparent however in the production reports from the furnace used.

The individual resistance furnaces were used in the early stages of experimental work at Iowa State College simply for convenience and speed in installation. As built they did not supply sufficiently uniform heating nor did they have sufficient capacity. They were abandoned as soon as the gas equipment could be procured and installed.

The low-frequency induction furnaces were used elsewhere and data are not available regarding their performance. However, the achievement of uniform heating over the length of the bomb offered considerable difficulty and pits and burn-outs seem to have resulted at a high rate.

The use of individual gas-heated furnaces has worked satisfactorily at one plant, although the maintenance of uniform heating is more difficult than with a larger installation.

The first planned production at Iowa State College called for a large soaking-pit in which a number of bombs could be heated. Such a pit was most economical in construction and gas comsumption and because of its large capacity was more easily maintained at constant temperature when bombs were introduced or removed. Such a plant was installed as described above and was thus duplicated at another site after a trial of the individual gas furnaces and an investigation of other types.

7. Properties of the Metal Produced

Many of the properties of uranium such as melting point, density, etc. recorded in the pre-project literature were erroneous and have been corrected by project experience. These results are recorded in Chap. VI, Vol. XII and in Chap. ___ Vol. XI A of M.P.R. Many properties of the metal are influenced by the method of preparation, however, and some of these properties, particularly those whose specifications were fixed will be discussed here.

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7.1 Density. The density of the metal was affected by variations in production and casting. Since low density usually meant blow-holes in the billet, density was used as a check on solidity and freedom from internal imperfections. The Ames metal varied in density from about 18.5 to 19.1 g/cc and averaged 18.9 g/cc during the greater part of the production period.

7.2 Purity. Since the content of certain elements could not be permitted to exceed fixed values which were less by several orders of magnitude than had ever before been customary in large scale metal production, analytical control of the composition of the final metal was very exact. The accepted standards and the average content of some of these elements, particularly those most necessarily kept under control at the metal production stage, are described here.

7.2.1 Boron. The most important of these elements was boron. In early production the boron content fluctuated considerably being derived at times from all of the different raw materials but particularly from the liner. It reached a peak in the summer of 1943 varying from 0.1 to 1.2 ppm averaging 0.31 ppm. A successful solution of the liner problem both by improvements in materials and installation reduced this content to an average of 0.22 ppm in the winter of 1943 from which it decreased gradually to an average of only 0.15 ppm in the fall of 1944.

Iron. The next most troublesome contaminant was iron derived largely from the pitting of the bombs, again due to poor liners. The solution of the liner problem reduced the iron from a high of 94 ppm average for the winter of 1943 to 57 ppm for the spring of 1944 to 46 ppm for the remainder of production.

Manganese. The manganese content was kept under observation because of its presence in some of the materials. However, it never became excessive ranging from 0 to Ca. 10 ppm, averaging 5 ppm during the latter part of production.

Cadmium. Cadmium was carefully controlled in the raw materials but was never excessive in the metal. In fact the use of some cadmium-high magnesium demonstrated the fact that Cd was distilled out during the vacuum melting and constituted little danger in the process. All the metal produced contained < 0.3 ppm, the accepted limit.

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To summarize, the major portion of the metal produced at Ames by the reduction of UF_4 by Mg had a density of 18.9 g/cc with the following average impurities: B, 0.22 ppm; Fe, 46 ppm; Mn, 25 ppm; Cd, < 0.3 ppm (probably < 0.2 ppm).

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